AL.2.1981-[illegible]

AOSTRA TECHNICAL PUBLICATION SERIES #4

OIL SANDS
COMPOSITION AND BEHAVIOUR RESEARCH

THE RESEARCH PAPERS
OF JOHN A. BICHARD
1957-1965

Alberta
OIL SANDS TECHNOLOGY
AND RESEARCH AUTHORITY

National Library
of Canada
Bibliothèque nationale
du Canada

CANADIANA

MAY 14 1991

OIL SANDS COMPOSITION AND BEHAVIOUR RESEARCH

JOHN A BICHARD

RESEARCH DEPARTMENT
IMPERIAL OIL LIMITED

SPONSORED BY
IMPERIAL OIL LIMITED
AND
SYNCRUDE OF CANADA LTD

PUBLISHED BY
ALBERTA OIL SANDS TECHNOLOGY & RESEARCH AUTHORITY (AOSTRA)

Edmonton 1987

ISBN Bichard 0 7732 0045 2

Digitized by the Internet Archive
in 2015

https://archive.org/details/oilsandscomposit00bich

OIL SANDS COMPOSITION AND BEHAVIOUR RESEARCH

The Research Papers
of
John A. Bichard
1957 - 1965

The results represented in this book are the sole responsibility of the author and AOSTRA makes no warranty as to their accuracy or usefulness for any purpose.

Published by

Alberta
OIL SANDS TECHNOLOGY
AND RESEARCH AUTHORITY

500, 10010 - 106 Street
Edmonton, Alberta, Canada
T5J 3L8

August 1987

PUBLISHER'S NOTE

AOSTRA TECHNICAL PUBLICATION SERIES
NUMBER 4

AOSTRA is pleased to publish this fourth book in a series of special publications by industry and academic authors. Like its predecessors *"Syncrude Analytical Procedures"*, *"The Thermodynamics and Transport Properties of Bitumens and Heavy Oils"*, and *"Aquathermolysis: A Synopsis of Work on the Chemical Reaction Between Water (Steam) and Heavy Oil Sands During Simulated Steam Stimulation"*, this publication is designed to make available, research results, analytical procedures, and engineering data on the properties and behaviour of Alberta petroleum resources that may otherwise not be available to the public.

M.A. Carrigy
Acting Chairman

Alberta Oil Sands Technology
and Research Authority

Edmonton, Alberta

December 1986

FOREWORD

During the 1950s and 1960s Mr. John A. Bichard, a research scientist with Imperial Oil Limited, undertook a comprehensive research program on the Alberta oil sands. Mr. Bichard began this investigation from a very fundamental viewpoint with a detailed analysis of the interactions among the individual solid, hydrocarbon, aqueous, and gaseous components associated with the oil sand structure. The work was done in support of the Syncrude Canada commercial oil sands project and the results were used as the basis for major process investigations undertaken by the Syncrude Canada Research Laboratory during the following two decades.

Mr. Bichard, Imperial Oil Limited, and Syncrude Canada Limited have agreed to make these original studies available to the research community interested in this field. The results of Mr. Bichard's work were issued as a series of individual company memoranda and have been reproduced in this volume essentially in their original form.

During the course of this work, the findings in the initial memoranda were frequently confirmed or modified in subsequent studies. This volume thus should be considered as the original notes from an active and distinguished researcher in this field. As a colleague of Mr. Bichard for almost three decades, I was continually astonished at the breadth of his research interests and the acumen he displayed in identifying the crucial data needed. This volume will be a valuable source of data for future researchers who are interested in one of the most exciting energy resources in Canada.

The support of the Alberta Oil Sands Technology and Research Authority, in keeping with its policy to make oil sands technology accessible to the public, is gratefully acknowledged.

C.W. Bowman

Table of Contents

i PREFACE

ii DESCRIPTION OF CONTENTS

I. COMPOSITION **1-1**
- 1. Oil Sands 1-1
- 2. Oil 1-1
- 3. Minerals 1-2
- 4. Water 1-2
- 5. Gas 1-2

II. BEHAVIOUR **1-2**
- 6. Flotation 1-2
- 7. Additives 1-3
- 8. Sand Reduction 1-3
- 9. Solvent Dilution 1-3

III. MECHANISMS **1-4**
- 10. Interfacial 1-4
- 11. Microstructure 1-4
- 12. Separations 1-4

I. COMPOSITION

1 OIL SANDS

1-1 Components **1-1**

1-2 Compositions **1-2**
- Oil 1-3
- Solids 1-3
- Water 1-3
- Salts and Ions 1-3
- Gas 1-3

1-3 Summary **1-7**

2 OIL

2.1 Physical Properties **2-1**
- 2-1-1 Oil Gravity and Viscosity 2-1
- 2-1-2 General Inspections 2-4

2-2 Chemical Composition **2-4**
- 2-2-1 Component Compositions 2-4

2-2-2 Polar Components 2-8
2-2-3 Adsorption on Solids 2-8
2-3 Aqueous Soluble Oil 2-11
2-3-1 Polar Solvents 2-11
2-3-2 Aqueous Solutions 2-11
2-3-3 Amphoteric Nature 2-16
2-3-4 Interfacial Dynamics 2-17
2-3-5 Soluble Oil 2-18
2-4 Solubility in Organic Solvents 2-21
2-4-1 General Solvency 2-21
(a) Theory 2-21
2-4-2 Critical Solubility Point 2-23
2-4-3 Specific Solvency 2-27
2-4-4 Solvent Solubility Parameters 2-30
2-4-5 Oil Component Solvency 2-30
2-5 Oil Structure 2-33
2-6 Summary 2-37

3 MINERALS

3-1 Total Solids 3-3
3-2 Light Minerals 3-3
3-2-1 Sand 3-5
3-2-2 Clay 3-7
3-2-3 Other Light Minerals 3-12
3-3 Heavy Minerals 3-13
3-3-1 Historical Background 3-13
3-3-2 Occurrence 3-17
(a) Size 3-17
(b) Non-Opaques 3-17
(c) Opaques 3-20
(d) Distribution 3-21
(e) Magnetic Minerals 3-24
3-3-3 Elements 3-26
(a) Majors 3-29
(b) Minors 3-29
(c) Analysis 3-29
3-3-4 Froth Solids 3-32
3-4 Reactive Minerals 3-34
3-4-1 Iron Reduced Minerals 3-34
3-4-2 Sulphide Oxidation 3-35
3-4-3 pH Effects 3-38
3-4-4 Clay pH Effects 3-42
3-4-5 Colloidal Material 3-42
3-5 Mineral Separation 3-44

4 WATER

4-1 Salt Content 4-4
4-1-1 Mineral Solubility 4-4
4-1-2 Soluble Salts 4-5
4-1-3 Amount of Salts 4-5
(a) Elements 4-5
(b) "Colloidal" Salt 4-6
(c) "Total" Salt 4-6
(d) "Maximum" Salts 4-6
(e) "Separations" Versus "Maximum" Salts 4-6
(f) Effect of pH 4-6
(g) Specific Conductance 4-8
(h) Sulphate Content Determines Acid pH 4-8
4-1-4 Summary 4-8
4-2 Polyvalent Ions 4-8
4-2-1 Mg and Ca Determinations 4-8
(a) Development of Techniques 4-15
(b) End Points 4-15
(c) Accuracy of Determination 4-15
(d) Development of Titration Technique 4-15
4-2-2 Ion Concentrations 4-17
4-2-3 Anion Effects 4-17
4-2-4 Separation Water Phases 4-17
4-2-5 Summary 4-21

4-3 Separations With Additives 4-21
  4-3-1 pH in Separation 4-21
    (a) Additive Solutions 4-25
    (b) pH Versus Specific Conductance 4-25
  4-3-2 Zeta Potential and Specific Conductance 4-25
    (a) Zeta Potential Measurements 4-25
    (b) Relationships in Hot Water Separation 4-25
    (c) Relationships with Addition of Chemicals 4-40
  4-3-3 Summary 4-40

5 GAS

II. BEHAVIOUR

6 FLOTATION

A. Original Beaker Experiments 6-2
6-1 Effects of Fines Without Aeration 6-2
6-2 Comparison with Pilot 6-2
  (a) Tumbler Tests 6-6
6-3 Variability of Oil Sands 6-6
6-4 Effect of Auguring 6-6
6-5 Behaviour of Blends 6-11
  (a) Separation Series I 6-11
  (b) Separation Series II 6-11
6-6 Effect of Freezing 6-11
6-7 Fines-Mixing Intensity 6-14
  (a) Mixing Intensity 6-14
  (b) Comparison of Results 6-22
6-8 Multiple Skimmings 6-26
  (a) Progressive or Staged Skimming of Froth 6-26
6-9 Aeration Rate 6-26
    (a) Flotation Gas 6-30
6-10 Separation pH 6-30

B. Pot Experiments 6-35
6-11 Water Addition 6-35
6-12 Mixing 6-41
  (a) Effect of Varying Feed Rate 6-41
  (b) Mixing Time 6-41
  (c) Cold Premixing Tar Sands With Water 6-41
6-13 Aeration Studies 6-43
  (a) Equivalent Air Volume at Different Rates 6-43
  (b) Effect of Multiple Aerations 6-43
  (c) Effect of Air Rate on Separation Using Different Tar Sands . . . 6-43
  (d) A Linear Plot With Log of Air Rate 6-46
  (e) Fresh Spot Samples 6-46
6-14 Temperature 6-46
6-15 pH Effect 6-59
6-16 Effect of Oil Content 6-59
6-17 Effect of Fines 6-59
6-18 Iron Content 6-59
6-19 Pilot Comparison 6-61
6-20 Summary 6-61

C. Process Control Evaluation 6-61
6-21 Oil Sands Classification 6-61
6-22 Process Energy Input 6-61
6-23 Selective Mining 6-72
6-24 pH Control 6-76

- **6-25 Divalent Metal Ions** . . . **6-78**
  - (a) Naturally Occurring . . . 6-78
  - (b) Acid Separations . . . 6-78
  - (c) Addition in Separation . . . 6-78
- **6-26 Correcting Processability** . . . **6-78**
- **6-27 Summary** . . . **6-92**
  - (a) Water Addition . . . 6-93
  - (b) Mixing . . . 6-93
  - (c) Aeration . . . 6-93
  - (d) Temperature . . . 6-94
  - (e) Processing of Tar Sands . . . 6-94
  - (f) Some Optimum Conditions for Separation . . . 6-94

7 ADDITIVES

A. Literature Studies . . . 7-1

B. Inorganic Additives . . . 7-2

- **7-1 Original Beaker Studies** . . . **7-2**
- **7-2 Reducing Agents** . . . **7-4**
- **7-3 A Lean Hole 11 Tar Sand** . . . **7-6**
  - (a) Emulsion Reversal . . . 7-6
  - (b) Summary . . . 7-6
- **7-4 A Rich Hole 11 Tar Sand** . . . **7-10**
- **7-5 A Low Oil-High Clay Tar Sand** . . . **7-10**
- **7-6 Miscellaneous Tar Sands** . . . **7-16**
- **7-7 Silicates and Phosphates** . . . **7-16**
  - (a) Sodium Silicates . . . 7-16
  - (b) Sodium Phosphates . . . 7-20
  - (c) Hole 11 Oil Sand . . . 7-20
  - (d) pH Effect . . . 7-23
  - (e) Zeta-Potential Effect . . . 7-23
- **7-8 Comparison of Sodium Salts** . . . **7-29**
  - (a) A More Comprehensive Study . . . 7-29
  - (b) Summary . . . 7-40
- **7-9 Pre-Washing Studies** . . . **7-40**
  - (a) Water Soluble Salts . . . 7-45
  - (b) Oil Soluble Component . . . 7-45
  - (a) Soaking . . . 7-47
- **7-10 Basis For Chemical Addition** . . . **7-47**

C. Organic Additives . . . 7-47

- **7-11 Sodium Oxalate** . . . **7-49**
- **7-12 Pyridine** . . . **7-53**
- **7-13 Surfactants** . . . **7-53**
- **7-14 Hydrophile-Lypophile Balance (HLB)** . . . **7-54**
- **7-15 Chelating-Complexing** . . . **7-54**
- **7-16 Summary** . . . **7-57**

8 SAND REDUCTION

- **8-1 Oil Agglomeration** . . . **8-1**
  - 8-1-1 Original Experiments . . . 8-1
  - 8-1-2 Water in Mixing . . . 8-4
  - 8-1-3 Connate Water . . . 8-7
  - 8-1-4 Agglomeration Mechanism . . . 8-7
  - 8-1-5 Temperature . . . 8-9
    - (a) Flexibility in Sand Reduction . . . 8-9
  - 8-1-6 Clay/Water Recycle . . . 8-9
  - 8-1-7 Coke Addition . . . 8-12
  - 8-1-8 Chemical Adjustment . . . 8-12
- **8-2 Agglomerate Separation** . . . **8-18**
  - 8-2-1 Mechanical . . . 8-18
    - (a) Submerged Screening . . . 8-18
    - (b) Moving Belt . . . 8-18
  - 8-2-2 Flotation . . . 8-22
    - (a) Reduced Pressure . . . 8-22

(b) Hydrocarbon Gas Flotation 8-30
(c) Denser Media Flotation 8-30

8-3 Continuous Processing 8-33

8-3-1 Mixer Designs 8-33
8-3-2 Demonstrations 8-33
(a) Helix and Submerged Rotary Screen 8-33
(b) Intermeshing Screw 8-33
(c) Pug Mill 8-36

8-4 Comparison with Hot Water Separation 8-38

8-5 Agglomerate Processing 8-38

8-5-1 Water Content 8-38
8-5-2 Coking Agglomerates 8-39

8-6 Economics and Conclusions 8-39

8-7 Summary 8-39

9 SOLVENT DILUTION

9-1 Settling Rates 9-3

9-1-1 Effect of Oil 9-3
9-1-2 Solvent Selection 9-3
9-1-3 Solution Rates 9-8

9-2 Froth Upgrading 9-8

9-2-1 Water Washing 9-13
9-2-2 Solvent Dilution 9-13
9-2-3 Inorganic Additives 9-16
9-2-4 Organic Additives 9-19
9-2-5 Summary 9-21

9-3 Agglomerate Upgrading 9-22

9-3-1 Solvent Dilution 9-22
9-3-2 Other Solvents 9-25

9-4 Membranes 9-25

9-4-1 Occurrence 9-25
9-4-2 Behaviour 9-26
9-4-3 Organic Component 9-26
9-4-4 Inorganic Components 9-27
9-4-5 Summary 9-27

9-5 Separation Techniques 9-27

9-5-1 Centrifuging 9-27
9-5-2 Ultrasonics 9-29
9-5-3 Electrostatics 9-31
9-5-4 Mechanical 9-31
9-5-5 Vibrating Screen 9-31
9-5-6 Comparison of Methods 9-34
9-5-7 Chemicals 9-34
9-5-8 Summary 9-34

9-6 A Continuous Solvent Dilution Process 9-35

9-6-1 General Conditions 9-35
(a) Separation Time 9-35
(b) Particle Size 9-35
(c) Solvent to Oil Ratio 9-35
9-6-2 Chemical Addition 9-35
(a) Carbonates and Silicates 9-35
(b) Effect of pH 9-37
(c) Effect of Concentration 9-37
(d) Effect of Breaxit Addition 9-37
(e) Miscellaneous Separations 9-37
9-6-3 Optimum Energy in Mixing 9-37
9-6-4 Solids in Separated Oil 9-40
9-6-5 Water in Separated Oil 9-40
9-6-6 A Three Stream Operation (Figure 9-18) 9-40
9-6-7 Projected Results 9-42
9-6-8 Summary 9-42

III. MECHANISMS

10 INTERFACIAL

10-1 Surface Energies 10-1
10-1-1 Surface Tension 10-3
10-1-2 Interfacial Tension 10-3
10-1-3 Effect of pH 10-6
10-1-4 Contact Angles 10-6
(a) Advancing 10-6
(b) Receding 10-6
(c) Water Phase 10-11
10-1-5 Work of Adhesion 10-11
10-1-6 Adhesion Tension 10-11
10-1-7 Settling Volumes 10-11
10-1-8 Conditions for Wetting 10-14
10-1-9 Spreading Coefficients 10-16
10-1-10 Summary 10-16
10-2 Zeta Potential 10-17
10-2-1 Concept 10-17
10-2-2 Oil Particles 10-17
10-2-3 Oil/Salt Effects 10-18
10-2-4 Pure Minerals 10-18
10-2-5 Mineral Suspensions 10-18
10-2-6 Cation Effects 10-21
10-2-7 Anion Effects 10-21
10-2-8 Aqueous Properties 10-23
10-2-9 Relation to pH 10-25
10-2-10 Specific Conductance 10-25
10-2-11 Clay Flocculation 10-25
10-2-12 Air Bubbles 10-25
10-2-13 Summary 10-25

11 MICROSTRUCTURE

11-1 Phase Relationships 11-2
(a) High Grades 11-2
(b) Low Grades 11-2
11-2 "Aging" 11-2
11-3 Oxidation 11-4
11-4 Implications 11-8
11-5 General Summary 11-8

12 SEPARATIONS SUMMARY

12-1 Oil Sand Grades 12-1
12-2 Hot Water Flotation 12-3
12-3 Mixing (Shear) 12-3
12-3-1 Design 12-3
12-3-2 Conditioning 12-3
12-3-3 Surfactants 12-6
12-3-4 Air Attachment 12-6
12-3-5 Clay 12-9
12-3-6 Temperature 12-12
12-3-7 Lower Grades 12-12
12-4 Primary Separation 12-12
12-4-1 Sand Removal 12-12
12-4-2 Froth Formation 12-14
12-5 Secondary Separation 12-14
12-6 Sand Reduction 12-14
12-7 Solvent Processes 12-14

IV. CONCLUSION

V. APPENDICES

V1 HOT WATER FLOTATION PARAMETERS

V2 INORGANIC ADDITIVES IN SLURRYING

V3 ORGANIC ADDITIVES IN SLURRYING

V4 SAND REDUCTION SEPARATIONS

V5 SOLVENT DILUTION CLEAN UP OF OIL

V6 EXPERIMENTAL TECHNIQUES AND EQUIPMENT

- **1. Tar Sand Sample Preparation and Storage** 1-1
  - (a) Preparation 1-1
  - (b) Storage 1-2
- **2. Tar Sand Composition** 1-2
- **3. Froth Composition** 1-4
- **4. Water Phase Composition** 1-4
- **5. Sand Phase Composition** 1-4
- **6. Solids Distribution** 1-4
- **7. Pot Method of Flotation** 1-4
- **8. pH Measurements** 1-9
- **9. Zeta Potentials** 1-15
- **10. U. V. Fluorescence** 1-15
- **11. Electrophoretic Studies** 1-19
- **12. Surface Tension of Oil** 1-19
- **13. Interfacial Tension of Oil** 1-19
- **14. Contact Angles** 1-21
- **15. Interfacial Viscosity** 1-21
- **16. Heavy Minerals** 1-21
- **17. 5µ and Less Material** 1-21
- **18. Other Analyses** 1-21
  - (a) Saturates-Aromatics-Resins-Asphaltenes (SARA) 1-21
  - (b) Infrared 1-29
  - (c) Differential Thermal Analysis 1-29
  - (d) Nuclear Magnetic Resonance 1-29
  - (e) X-Ray 1-29
  - (f) Elemental Analysis 1-29

V7 ORIGINAL BEAKER FLOTATION EXPERIMENTS

- **1. Effect of Fines With No Aeration** 1-1
- **2. Modified Beaker Technique** 1-2
- **3. Training** 1-3

V8 SOLVENT EXTRACTION

1. Electrostatic Separation 1-1
(a) Separation of Tar Sand 1-3
(b) Separation of Froth. 1-3
(c) Summary 1-8
2. Solvent /Dilution and Settling. 1-8
(a) Other Solvent Studies. 1-8

VI. ACKNOWLEDGEMENTS

VI ACKNOWLEDGMENTS

List of Tables & Figures

i FOREWORD

ii DESCRIPTION OF CONTENTS

1. COMPOSITION

OIL SANDS

Table 1-1 The Components of the Tar Sands 1-3
Figure 1-1 Oil Sands Composition 1-4
Table 1-2 General Inspections on Tar Sand Characterization samples 1-5
Figure 1-2 Correlation of Oil Sand Composition 1-6
Table 1-4 Classification of Type and General Inspections on Beaver River Tar Sands used in Studies 1-7
Table 1-3 Fines (Clay Minerals) can be mostly in Lenses or strata 1-7

2 OIL

Table 2-1 Quality Comparison with Conventional Crudes 2-2
Table 2-2 Gravities of Oils Extracted from Mildred Lake Tar Sands 2-2
Figure 2-1 Gravity-Viscosity at 210°F Relationship for Oil from the Athabasca Tar Sands (both measurements corrected for ash contents) 2-3
Figure 2-2 Relative Density Relationship for Water and Oil from Mildred Lake Tar Sand 2-5
Table 2-3 Inspections on Oils 2-6
Table 2-4 Inspections Extracted Oil (1) from Characterization Tar Sands . . . 2-7
Figure 2-3 Infrared Adsorption Spectra of Toluene Extracted Oil from Hole 11 Tar Sand Containing 0.5 Material 2-8
Table 2-5 Composition of Oil Components from Characterization Tar Sands Attapulgus Clay Separations 2-9
Table 2-6 Inspections on Oil and on Alphaltene Component from Characterization Tar Sands 2-10
Figure 2-4 Relative Fluorescence of Acid and Base Solutions in contact with Oil at Different Temperatures 2-12

Figure 2-5 Relative Fluorescence of Acid and Base Solutions in contact with Oil at Different Temperatures 2-13
Figure 2-6 Effect on pH of Acid and Base Solutions in contact with Oil at Different Temperatures 2-14
Figure 2-7 Fluorescence Behaviour of Acid and Base Soluble Components of Oil 2-15
Figure 2-8 Infrared Spectra of an Extracted Base Soluble Oil (Extracted from Area B with a 11.5 pH - NaOH Solution) 2-16
Figure 2-9 Infrared Spectra of an Extracted Acid Soluble Oil (Extracted from Hole 11 with a 1.5 pH - HCL Solution) 2-17
Table 2-7 Relative Fluorescence of Separated Water Phase after Removal of Fines(1) 2-19
Figure 2-10 Effect of pH on the Amount of Dissolved, Micelle or Colloidal Oil Water Phase (0.2 m) 2-20
Table 2-8 Oil Component of Water Phase(1) 2-22
Figure 2-11 Infrared Analysis of Extracted Oil from Water 2-23
Figure 2-12 A General Athabasca Oil Composition 2-24
Figure 2-13 General Oil Solubility 2-24
Table 2-9 Factor in Solubility Theory 2-25
Figure 2-14 Interpretation of Solubility Results 2-26
Figure 2-15 Y-Axis Intercept Is Characteristic of a Particular Solvent 2-28
Figure 2-16 Y-Axis Intercept Is Characteristic of a Particular Solvent 2-28
Figure 2-17 Solvent Transposition Procedure 2-28
Figure 2-18 Pure Hydrocarbons 2-29
Figure 2-19 More Polar Solvents 2-29
Figure 2-20 Typical Refinery Hydrocarbon Mixtures 2-29
Figure 2-21 Hydrocarbons Relative to Deodorized Varsol 2-29
Table 2-10 Solubility Parameter Summary and Comparison 2-31
Figure 2-22 Solubility Parameter Correlation Exists Only for Non-Polar or Weakly Polar Solvents 2-31
Figure 2-23 Low Boiling Aromatics Are Better Solvents at Low Mixing Efficiency 2-32
Figure 2-24 Relationship of Interfacial Tension and Solvent Power 2-34
Table 2-11 Oil Component Solubility Parameters 2-35
Figure 2-25 Silica Gel Separation 2-35
Figure 2-26 Attapulgus Clay & Silica Gel Separation 2-35
Figure 2-27 Asphaltene Concentration Effect 2-35
Table 2-12 Oil Component Order in Oil Micelle Structure 2-36

3 MINERALS

Table 3-1 Minerals in the Oil Sands 3-2
Figure 3-1 Solids Distribution as a Function of Size and Density (Beaver Creek Solids) 3-4
Figure 3-2 Sand Size Distribution 3-6
Table 3-2 Inspections on Tar Sand Characterization Samples and Extracted Solids 3-7
Figure 3-3 (a) Differential Thermal Analysis Patterns on 5m and Less Material from Area B, Holes 11 and 21A 3-9
Figure 3-3 (b) Differential Thermal Analysis Patterns on 5m and Less Material From Core Hole 15-16-2 3-9
Figure 3-3 (c) Differential Thermal Analysis Patterns on 5m and Less Material From Core Hole 29-16-2 3-10
Figure 3-3 (d) Differential Thermal Analysis Patterns on 5m and Less Material From Core Hole 33-14-2 3-10
Figure 3-4 Differential Thermal Analysis Patterns for Some Reference Clay Samples 3-11
Table 3-3 X-Ray Diffraction of Clays 3-12
Table 3-4 Heavy Minerals reported in Literature on Athabasca Tar Sands Reference 3-14
Table 3-5 Summary of Existing Analyses of Tar Sand Heavy Minerals 3-15
Figure 3-5 Map of Sample Locations 3-16
Figure 3-6 Frequency Distribution of Weight Percentages 3-18
Figure 3-7 Size Distribution of Solids and Heavy Minerals 3-19

Table 3-6 Heavy Mineral Content of Tar Sand Samples 3-20
Table 3-7 Amount and Emission Spectrographs on Denser Mineral fractions 3-21
Table 3-8 Non-opaque Heavy Minerals 3-22
Table 3-9 Opaque Heavy Mineral Oxides 3-23
Figure 3-8 Mineral Gravity Distibution in Total Heavy Minerals Extracted from Beaver Creek Tar Sands 3-25
Figure 3-9 A General Description of Minerals from Gravity Fractionation of Beaver Creek Tar Sands 3-27
Table 3-10 Emission Spectrograph Analyses of Heavy Minerals 3-28
Table 3-11 Emission Spectrograph Analysis of Heavy Minerals 3-28
Table 3-12 Miscellaneous Emission Spectrographs Analyses of Heavy Mineral Fractions 3-30
Table 3-13 Emission Spectrograph Analyses of Heavy Minerals 3-31
Table 3-14 Occurrence of Manganese 3-33
Table 3-15 Solids and Heavy Mineral Removal in Different Process Stages 3-35
Table 3-16 Gravity Fractionation* of Solids from a Beaver Creek Froth Separated without Aeration 3-36
Table 3-17 Opaque Heavy Mineral Sulphides and Carbonates 3-37
Table 3-18 Sulphide and Carbonate occurrence in Heavy Minerals 3-38
Table 3-19 Soluble Material from Concentrated Hydrogen Peroxide and Acid Treating 3-39
Table 3-20 Other Treatment Studies 3-40
Table 3-21 pH of some Minerals in Aqueous Suspension 3-41
Table 3-22 pH Changes of Heavy Minerals 3-43
Table 3-23 Water Phase Exhibits Same pH as Tar Sand 3-43
Table 3-24 pH of "Clay" Varies 3-43
Table 3-25 Solid Dispersion Increase with pH in Range 8-10 3-45
Table 3-26 Colloidal Salt Decreases with pH 3-45
Table 3-27 Summary of some Mineral Factors affecting Oil Sand pH and Processability 3-45

4 WATER

Table 4-1 Capillary - a Function of Grain Diameter not affected by Drainage(39) 4-2
Table 4-2 Calculated Solubility in Water at 25-30°C-% 4-2
Figure 4-1 Effect of Temperature on the Solubility of Quartz (A) and Amorphous Silica (B) (Literature Data) 4-3
Table 4-3 Soluble Salt Content of Tar Sands 4-4
Table 4-4 Emission Spectrographic Analyses for Components of Salt Dissolved in the Water Phase 4-7
Figure 4-2 Examples of Water Washing Tar Sands 4-9
Figure 4-3 Effect of Number of Washings on Soluble Salt Content 4-10
Figure 4-4 Effect of Number of Washings on Colloidal Salt Content 4-11
Figure 4-5 Salt Content Increases with Decreasing pH 4-12
Figure 4-6 Effect of Soluble Salt and Precipitated (colloidal) Salt on Water Phase Conductance 4-13
Figure 4-7 Free Sulphuric Acid from Oxidation of Metal Sulphides and Hydrolysis of the Resulting Sulphates Procedures Tar Sand Acidity 4-14
Table 4-5 Effect of pH , Temperature, and Time on Precipitation of Calcium and Magnesium Hydroxides 4-16
Table 4-6 Only Tripolyphosphate Sequesteres Calcium 4-17
Figure 4-8 Effect of Sample Size, Interfering Ions and Sodium Hydroxide Addition in Titrimetry for Calcium and Magnesium 4-18
Figure 4-9 Determination of Calcium and Magnesium Ion Concentrations in Water Phases Using Ethylendiamine Tetraacetate Titration 4-19
Figure 4-10 Precipitation of Calcium and Magnesium Occurs Only at High pH, Temperature and with Longer Contact Times 4-20
Figure 4-11 The Amount of Soluble Calcium and Magnesium in the Separation Water Phase Varies with pH 4-22
Table 4-7 Magnesium and Calcium Contents of Separated Water Phases as determined by Ethlenediamine Tetraacetate Titrations 4-23

Figure 4-12 Relationships of pH for Different Water Phases 4-24
Figure 4-13 Relationship of Concentration of Sodium Salts and Specific Conductance of Solution 4-26
Figure 4-14 Relationship of pH and Specific Conductance for Fine Solids Suspensions in Different Sodium Salt Solutions 4-27
Figure 4-15 Sodium Salt Concentrations vs. pH of Solutions Used to Obtain Zeta Potential and Specific Conductance Measurements 4-28
Figure 4-16 Specific Conductance and pH Relationship of Centrifuged Water Phase 4-29
Figure 4-17 Relationship of Zeta Potential of Fine Solids in Different Water Phases 4-30
Figure 4-18 Relationship of pH and Zeta Potential of Various Beaver River Tar Sands 4-31
Figure 4-19 Zeta Potential as a Function of Specific Conductance of Water Phase . 4-32
Table 4-8 Measurements on Sodium Salt Solutions containing a drop of Water Phase from Hot Water separation of Bench Unit Feed-run No. 9 Tar Sand 4-33
Figure 4-20 Relationship of Zeta Potential of Fine Solids in Different Water Phases 4-34
Figure 4-21 Relationship of pH and Zeta Potential of Fine Solid Suspensions in Different Sodium Salt Solutions 4-35
Figure 4-22 Specific Conductance and Zeta Potential Relationship of Centrifuged Water Phase 4-36
Figure 4-23 pH and Zeta Potential (ZP2) Relationship 4-37
Figure 4-24 Specific Conductance and Zeta Potential Relationship 4-38
Figure 4-25 pH and Zeta Potential (ZP1) Relationship 4-39

5 GAS

II. BEHAVIOUR

6 FLOTATION

Table 6-1 Effect of Clay in Hot Water Separation (Initial Beaker Experiments) . 6-3
Figure 6-1 Effect of Clay on Oil Recovery in Hot Water Process (Initial Beaker Experiments) 6-4
Table 6-2 A Comparison of Tar Sand Separations in the CSAI Bench Unit and Imperial's Laboratory Technique (Good Quality Tar Sand - Area "B")(4) 6-5
Table 6-3 A Comparison of Tar Sand Separations in the CSAI Bench Unit and Imperial's Laboratory Technique (Medium to Poor Quality Tar Sand - Location "D"- Area of #9 Auger Hole) 6-7
Table 6-4 Laboratory Extraction Technique Can Be Adapted to Study Process Variables in the Bench Unit such as Evaluation of Tumbler Effluent . 6-8
Table 6-5 Preliminary Study of Processability of Tar Sand from Core 22A-7 . . 6-9
Table 6-6 Comparision of Laboratory Dense Phase Extractions of Spot Samples Taken from Area "D" in the Area of Auger Hole No. 9 6-10
Figure 6-2 Oil Recovery Is General Function of Tar Sand Grade 6-12
Table 6-7 Laboratory Extraction Comparision of Augered and Hand Dug Samples of Tar Sands from the Sample Location 6-13
Table 6-8 Summary of Laboratory Dense Phase Separation Results (Series I) with Blends of Tar Sands from Area "B" and "D" 6-15
Figure 6-3 Laboratory Dense Phase Separations (Series I) of Blends of Poor Quality Area "D" and an Area "B" Tar Sands 6-16
Table 6-9 Summary of Laboratory Dense Phase Separation Results (Series I) with Blends of Tar Sands from Area "B" and "D" 6-17
Figure 6-4 Laboratory Dense Phase Separations (Series II) of Blends of Poor Quality Area "D" and an Area "B" Tar Sands 6-18

Table 6-10 Preliminary Results on Effect of Freezing Tar Sand Feed prior to Separation in a Dense Phase Operation . . . 6-19
Table 6-11 Effect of Clay and Mixing in Hot Water Separation with Aeration (Tar Sand contained 1.7 Wt % Oil, 2.2 Wt % Water, 80.4 Wt % Sand, 5.7 Wt % Clay) . . . 6-20
Table 6-12 Effect of Clay and Mixing in Hot Water Separation with Aeration (Tar Sand contained 11.7 Wt % Oil, 2.2 Wt % Water, 80.4 Wt % Sand, 5.7 Wt % Clay) . . . 6-21
Table 6-13 Froth Quality from Hot Water Separations with Good Quality Tar Sands . . . 6-22
Figure 6-5 High Clay and Severe Mixing with Aeration Give Poor Oil Recoveries (Tar Sand Contained 11.7 Wt % Oil, 2.2 Wt % Water, 80.4 Wt % Sand, and 5.6 Wt % Clay) . . . 6-23
Figure 6-6 More Severe Mixing Emulsifies Water in Froth, and Froth Composition Is Independent of Added Clay (Tar Sand Contained 11.7 Wt % Oil, 2.2 Wt % Water, 80.4 Wt % Sand, and 5.7 Wt % Clay) . . . 6-24
Figure 6-7 More Severe Mixing Emulsifies Water in Froth, and Solids Content Is Independent of Mixing and Aeration (Clay Addition and Aeration Experiments) (Tar Sand Contained 11.7 Wt % Oil, 2.2 Wt % Water, 80.4 Wt % Sand, and 5.7 Wt % Clay) Sieve . . . 6-25
Figure 6-8 Progressive Skimmings Improve Oil Recoveries in a Given Separation Time (Tar Sand Contained 11.7 Wt% Oil, 2.2 Wt% Water, 80.4 Wt% Sand, and 3.7 Wt% Clay) . . . 6-27
Table 6-14 Effect of Skimming and Aeration in Hot Water Separations (An Area B Tar Sand containing 11.7 Wt % Oil, 2.2 Wt %Water, 80.4 Wt % Sand and 5.7 Wt % Clay) . . . 6-28
Figure 6-9 Higher Aeration Rates and Frequent Skimmings Improve Oil Recoveries in a Given Separation Time (Tar Sand Contained 11.7 Wt % Oil, 2.2 Wt % Water, 80.4 Wt % Sand, and 5.7 Wt % Clay*) . . . 6-29
Table 6-15 Summary of "Quicky" Experiments to Show the Affect +of Aeration (with mixing) Time and Air Rate in Hot Water Separation of Area B Tar Sand . . . 6-31
Figure 6-10 Froth composition . . . 6-32
Figure 6-11 Air Rate . . . 6-33
Figure 6-12 Water in Oil Emulsification Increases with Aeration Time : Tar Sand Storage Results in water Loss and Oil-Solid wetting . . . 6-34
Table 6-16 Effect of Gas Treatment prior to and during Hot Water Separation (Tar Sand from Area "D" contained 11.1% Water, 9.7% Oil, and 79.2%solids) . . . 6-36
Table 6-17 Methane vs. Air as a Flotation Gas (Bad Beaver Creek Tar Sand) . . . 6-37
Table 6-18 Comparision of Processability of Tar Sand Samples from Different Locations at Mildred Lake . . . 6-38
Table 6-19 Effect of Water in Mixing with a High Water area B Tar Sands (Aeration in Separation) . . . 6-39
Table 6-20 Effect of Water in Mixing with an aged Area B Tar Sands . . . 6-39
Table 6-21 Effect of Water in Mixing with an Area D Tar Sand . . . 6-39
Table 6-22 Effect of Minimum Slurry and Standard Water in Mixing . . . 6-40
Table 6-23 Effect of High Total Water with an Area D Hole 10 Tar Sand . . . 6-40
Table 6-24 Effect of Mixing Intensity with an Area B Tar Sand . . . 6-40
Table 6-25 Solids Distribution in Froth . . . 6-42
Table 6-26 Effect of Charge or Mixing Intensity with an Area D Hole 10 tar Sands (2 Aerations of 5 in at 2.0 Cubic ft/hr) . . . 6-42
Table 6-27 Effect of Mixing Time with Area B Tar Sand . . . 6-42
Table 6-28 Effect of Mixing Time with an Area D Hole 11 Tar Sand . . . 6-44
Table 6-29 Effect of Aeration Time and Equivalent Air Volume at Different Rates 6-44
Table 6-30 Effect of One vs. Two Aeratrions . . . 6-44
Table 6-31 Reproducibility and Temperature Studies (Brass Pot) with a Sample (#1) of Homogenized Bench Unit Tar Sands Feed . . . 6-45
Table 6-32 Solids in Froth Decrease Slightly with Increasing Temperature . . . 6-46

Figure 6-13 Oil Recovery as a Function of Air Rate for Tar Sands of Different Quality . . . 6-49
Figure 6-14 Froth Composition as a Function of Air Rate for Tar Sands of Different Quality . . . 6-50
Figure 6-15 Good Quality Tar Sands - Area B - Gave High Oil Recoveries and Good Froth Qualities, Linear with Air Rate in the Range 0.1-3.5 cubic Feet/Hour . . . 6-51
Figure 6-16 Progressive Aeration Is Most Significant for High Oil Recoveries with Poor Quality Tar Sands - Area D, Hole 11 : Higher Air Rates Increased the Solids Content of the Froth . . . 6-52
Figure 6-17 Higher Air Rates and Progressive Aerations Gave High Oil Recoveries, but Poor Froth Quality with a Poor Quality Tar Sand - Area 4 . . . 6-53
Figure 6-18 Progressive Aeration Gave Higher Oil Recoveries with a Poor Quality Area D (Hole 9) . . . 6-54
Figure 6-19 Effect of Temperature on Froth Composition and Oil Recovery with an Area D (West of Hole 9) Tar Sand . . . 6-55
Figure 6-20 Effect of Temperature on Froth Composition and Oil Recovery with a High Water Area B Tar Sand . . . 6-56
Figure 6-21 Effect of Temperature on Froth Composition and Oil Recovery with an Area 4 Tar Sand . . . 6-57
Figure 6-22 Effect of Temperature on Froth Composition and Oil Recovery with an Area D Tar Sands from Cut Adjacent to Hole 9 . . . 6-58
Figure 6-23 Effect of Temperature on Froth Composition and Oil Recovery with Area D, Hole 11 Tar Sand . . . 6-60
Figure 6-24 Processability Is a Function of pH of Tar Sands . . . 6-62
Figure 6-25 Froth Composition Is Related to pH of the Tar Sands . . . 6-63
Figure 6-26 Fines in Area D Feeds Have a Significant Effect on Froth Quality . . . 6-64
Table 6-33 Hot Water Flotation Separations (Brass Pot) of Tar Sand Characterization Samples at Standard Conditions . . . 6-65
Table 6-34 Classification of Type and General Inspections on Beaver River Tar Sands used in Studies . . . 6-66
Figure 6-27 Effect of Sand State and Amount of Fines on Oil Recovery . . . 6-67
Figure 6-28 Preliminary Comparison of Hot Water Flotation Separations . . . 6-68
Table 6-35 Summary of Electrical, Chemical and Colloidal Parameters of the Water Phase from Separation of the Athabasca Tar Sands . . . 6-69
Table 6-36 Processability Summary of Beaver River Tar Sands . . . 6-70
Table 6-37 Effect of Mixing Speed on Tar Sand Processability (Beaver River Plant Feed : 11% Oil, 4% Water, 16% Clay, 69% Sand) . . . 6-71
Table 6-38 Three Stage Separation of Tar Sands . . . 6-72
Figure 6-29 Increasing Mixing Speed and Aeration Increases Oil Recovery . . . 6-73
Table 6-39 Effect of Clay on Processability of Beaver River Tar Sands (Plus 0.12 Wt % on Tar Sand Sodium Hydroxide Addition for pH Control) . . . 6-74
Table 6-40 Extreme pH effects on Processability of Tar Sands . . . 6-75
Table 6-41 Acid Separations gave High Ca + Mg Contents in the Separation Water Phaseand Poor Processability . . . 6-76
Table 6-42 Effect of Calcium and Magnesium Addition on Processability of Beaver River Plant Feed Tar Sands (0.08 Wt % on Tar Sand of Sodium Hydroxide was added in Mixing for pH Control) . . . 6-77
Figure 6-30 Increasing Mixing Speed Increases Water in Froth , and Increasing Aeration Increases both Water and Solids . . . 6-79
Figure 6-31 Relationship of Processability with Fines Content at a Constant pH of 9.9 . . . 6-80
Figure 6-32 Relationship of Processability with Oil Content at a Constant pH of 9.9 6-81
Figure 6-33 pH Effect on Processability of Beaver River Tar Sands (Primary Separation) . . . 6-82
Figure 6-34 pH Effect on Processability of Beaver River Tar Sands (Primary+ Secondary Separation) . . . 6-83

Figure 6-35 Relationship of Froth Contaminants to pH for Beaver River Tar Sands (Primary Separation) 6-84
Figure 6-36 Relationship of Froth Contaminants to pH for Beaver River Tar Sands (Primary + Secondary Separation) 6-85
Figure 6-37 Relationship of Froth Quality to Oil and Fines Contents of Feed at a Constant pH of 9.9 6-86
Figure 6-38 Processability of Bench No.1 Tar Sands Is Better in Acid Media Than Other Beaver River Tar Sands but Still Best at pH's 8-11 6-87
Figure 6-39 Inter-Relationship of Naturally Occurring Soluble Calcium and Magnesium in the Water Phase and Processability (variable pH) 6-88
Figure 6-40 Effect of Calcium Addition on Froth Quality of Beaver River Plant Feed Tar Sands at a Constant pH of 9.9 6-89
Figure 6-41 Effect of Calcium Addition and Relationship of Soluble Ions to Processability of Beaver River Plant Feed Tar Sand at a Constant pH 9.9 . . 6-90
Figure 6-42 Oil Recovery in Hot Water Flotation of Different Oil Sands with the Addition of Magnesium Salts and Sodium Hydroxide 6-91
Table 6-43 Complexing Agents Restores Processability in Optimum Alkaline Conditions of 9.5 pH 6-92

7 ADDITIVES

Table 7-1 Past Developments in Flotation Processes 7-1
Table 7-2 Summary of Small Scale Laboratory Hot Water Flotation Studies of American Oil Sands by U.S Bureau of Mines 7-3
Table 7-3 Effect of Salts in Hot Water Separation (Tar Sand from Area "D" contained 9.5% Water, 9.75% Oil and 80.75% Solids) 7-4
Table 7-4 Effect of pH in Hot Water Separation (Tar Sand from Area "D" contained 3.4% Water 11.9% Oil and 84.7% Solids) 7-5
Figure 7-1 Effect of a Reducing Agent (Stannous Chloride) and pH on Froth Quality 7-7
Figure 7-2 Comparison of Solids Reduction in the Froth of Various Agents . . . 7-7
Figure 7-3 Effect of Mixing Solution pH on Oil Recovery (Hole 11 - Lean) . . . 7-8
Figure 7-4 Effect of Final pH on Oil Recovery 7-8
Figure 7-5 Relation of Final and Mixing Solution pH's (Hole 11 - Lean) 7-9
Figure 7-6 Effect of pH on Solids to Oil Ratio in the Froth 7-9
Figure 7-7 Effect of Mixing Solution pH on Oil Recovery (Hole 11 - Rich) . . . 7-11
Figure 7-8 Effect of Final pH on Froth Composition 7-11
Figure 7-9 Effect of Mixing Solution pH on Froth Composition (Hole 11 - Rich) . 7-12
Figure 7-10 Effect of Final pH on Froth Composition 7-12
Figure 7-11 Relation of Final and Mixing Solution pH's (Hole 11 - Rich) 7-13
Figure 7-12 Effect of Sodium Salt Concentration on Oil Recovery (Hole 21A) . . 7-14
Figure 7-13 Effect of Sodium Salt Concentration on Oil Recovery (Hole 21A) . . 7-15
Table 7-5 Effect of Sodium Silicate of Different $Na_2O:SiO_2$ Ratios but Equivalent Sodium Content on a Hole 11 Tar Sand 7-17
Figure 7-14 Effect of Different Silicates on Processability of a Hole 11 Tar Sands . 7-18
Figure 7-15 Effect of Different Silicates on Processability of a Hole 11 Tar Sands . 7-19
Table 7-6 Decreasing Effectiveness of Phosphates for Sequestration of Calcium(45) 7-21
Table 7-7 Decreasing Effectiveness of Phosphates for Sequestration of Calcium(45) 7-21
Table 7-8 Sodium Tripolyphosphate is Superior to Dequest Phosphates 7-21
Figure 7-16 Effect of Sodium Phosphates and Concentration on Processability of a Poor Quality Tar Sand 7-22
Table 7-9 Zeta Potentials at Constant pH 7-23
Figure 7-17 (a) Effect of Sodium Phosphate Additives on Processability as a Function of pH 7-24
Figure 7-17 (b) Effect of Sodium Phosphate Additives on Processability as a Function of pH (Continued) 7-25

Figure 7-18 Relationship of Sodium Phosphate Additive and Concentration with pH 7-26
Figure 7-19 Relationship of Zeta Potential and pH of Water Phase For Different Sodium Phosphate Additives at Different Concentrations 7-27
Figure 7-20 Effect of Sodium Phosphate Addition on Processability as a Function of Zeta Potential 7-28
Table 7-10 Comparison of Hydroxide - Silicate - Tripolyphosphate 7-29
Figure 7-21 Chemical Adjusted Processability of Beaver River Tar Sands as a Function of Water Phase pH 7-31
Figure 7-22 Relationship of Processability to Specific Conductance of Water Phase 7-32
Figure 7-23 Relationship of Processability to Zeta Potential (ZP) 7-33
Figure 7-24 Relationship of Processability to Zeta Potential of Centrifuged Water Phase (ZP2) 7-34
Figure 7-25 Chemical Adjusted Processability of Beaver River Tar Sands as a Function of Water Phase pH 7-35
Figure 7-26 Oil Loss to Water Phase in Chemical Addition Separations as a Function of Water Phase pH 7-36
Figure 7-27 Oil Loss to Sand in Chemical Addition Separations as a Function of Water Phase pH 7-37
Figure 7-28 Solids-Oil in Froth with Chemical Addition as a Function of Water Phase pH 7-38
Figure 7-29 Solids-Oil Ratios in Froth from Chemical Addition as a Function of Water Phase pH 7-39
Figure 7-30 Water-Oil Ratios in Froth from Chemical Addition Separations as a Function of Water Phase pH 7-41
Figure 7-31 Relationship of S/O and W/O Ratios in Froth with Chemical Addition to Different Beaver River Tar Sands 7-42
Figure 7-32 Relationship of S/O and W/O Ratios in Froth with Chemical Addition to Different Beaver River Tar Sands 7-43
Table 7-11 Chemical Adjusted Processability of Beaver River Tar Sands 7-44
Table 7-12 Effect of Prewashing Tar Sands 7-46
Table 7-13 Effect of Soaking on Separation 7-46
Figure 7-33 Relationship between Oil Recovery with Phosphate Addition and Free Calcium Ions at Equivalent Concentration 7-48
Figure 7-34 Effect of Oxalate and pH on Oil Recovery 7-50
Figure 7-35 Effect of Oxalate and pH on Froth Composition 7-51
Figure 7-36 Effect of Oxalic Acid Addition at Constant Sodium Hydroxide Content (pH of Water Phase is Shown in Parenthesis) 7-52
Table 7-14 Effect of Pyridine Addition 7-53
Table 7-15 1963 Exploratory Data on the Effect of Surfactant Class Base Case : Hole 11 Lean (7.5% Oil) Plus NaOH/NaTPP (0.5/1.0 lbs per ton) at an Oil Rec. of 82% 7-55
Table 7-16 Simplified Explanation of Extractability Results (Without Inorganic Additives) 7-55
Figure 7-37 Data on the Effect of HLB Additives (Pot Extractions) 7-56
Figure 7-38 Processability as a Function of Zeta Potential (Unit Feed - Run No. 6 Tar Sand) 7-59
Figure 7-39 Processability as a Function of Zeta Potential in Distilled Water (Unit Feed - Run No. 6 Tar Sand) 7-60
Figure 7-40 Processability with Complexing Agent Additions (Unit Feed - Run No. 6 Tar Sand) 7-61
Figure 7-41 Zeta Potential - Specific Conductance Relationship at 9.3-10.0 pH . . 7-62
Figure 7-42 Processability with Complexing Additives (0.005 Wt % on Tar Sands) (Unit Feed - Run No. 6) 7-63
Figure 7-43 Processability with Complexing Additives (0.05 Wt % on Tar Sands) (Unit Feed - Run No. 6) 7-64
Figure 7-44 Froth Composition with Complexing Agent Addition 7-65

8 SAND REDUCTION

Figure 8-1 Sand Reduction 8-2
Table 8-1 Original Sand Reduction Experiments (Tar Sand Mixed with Water in a Motar with a Pestle at Room Temperature 100% Oil Recover (Est) . 8-3
Table 8-2 A Minimum Amount of Water is Required in Sand Reduction (Tar Sand No. O contained 5 Wt % Water and 15 Wt % Oil 8-3
Figure 8-2 An Optimum Amount of Water Gave Greatest Sand Reduction in Mixing 8-5
Figure 8-3 Effect of Tar Sands Water Content on Sand Reduction 8-6
Figure 8-4 Tar Sand Storage Decreases Potential for Sand Reduction 8-8
Figure 8-5 Sand Reduction and Oil Recovery Are Optimized by Operating Temperature with a High Water Content Tar Sands 75 Wt % Total Water: 5 Minutes Mixing 8-10
Figure 8-6 Effect of Temperature on Sand Reduction with a Low Water Content Tar Sands 75 Wt % Total Water : 5 Minutes Mixing 8-11
Table 8-3 Progressive Lowering of Temperature Gives Good Agglomeration and Sand Reduction (Tar Sand No. 3 contained 2 Wt % Connate Water) . 8-13
Table 8-4 Sand Reduction Experiments with "Carbon" Addition(7) Room Temperature Operations Essentially 100% Oil Recovery in Oil Phase . 8-13
Figure 8-7 Comparison of Effect of Clay on Oil Recovery in Sand Reduction and in Hot Water Separation Process 8-14
Figure 8-8 Clay in Recycle Water Has Little Effect on Agglomerate Quality . . 8-15
Figure 8-9 Effect of Fluid Coke Addition on Sand Reduction with a High Water Content Tar Sand 70-75 °F 5 Minutes Mixing 100 % Recovery . . . 8-16
Figure 8-10 Effect of Fluid Coke Addition and Temperature on Sand Reduction with a Low Water Content Tar Sand 25 Wt % Fluid Coke Addition: 5 Minutes Mixing: 100 % Oil Recovery 8-17
Table 8-5 Evaluation of Screen Shape (Tar Sands No. 11 30 lb/hr Run No. 24) 8-19
Table 8-6 A Flat Inclined Screen is Unsuitable for Separating Agglomerates and Sand (Tar Sand - 19a: Feed Rate - 120 lb/hr : Water/Feed Ratio - 0.75: Screen Area - 1.5 ft^2: Screen Slope - 38° to the Horizontal) 8-19
Figure 8-11 Relationship between Pug Mill Chute and Belt for Runs 8-14 8-20
Figure 8-12 Apparent Oil Phase and Associated Gas Volume Changes with Temperature and Pressure (Oil Phase Contained 74 Wt % Solids) . . 8-23
Figure 8-13 Temperature and Pressure Relation at which Oil-Phase Flotated on Water (Points Are Average of 2-6 Measurements) 8-24
Figure 8-14 Flotation of Agglomerates 8-26
Figure 8-15 Techniques of Separation Using Reduced Pressure 8-27
Figure 8-16 Oil Recovery from Area B Tar Sand 8-28
Figure 8-17 Oil Recovery from Area D Tar Sand 8-28
Table 8-7 Comparison of Separations Using Reduced Pressure Flotation and Submerged Screening (Mixed with 75 Wt % Water on Tar Sands (Dry Basis) at Room Temperature 70°F) 8-29
Figure 8-18 Separation by Fluidized Solids Flotation 8-31
Table 8-8 Preliminary Comparison of Continuous Methods of Separation (Tar Sand No. 11 ; 70°F) 8-32
Table 8-9 Belt Conveyor and Rotary Screen Are Equally Effective for Separating Agglomerates and Solids (Tar Sand - 19a: Feed Rate - 60 lb/hr: Water/Feed Ratio - 0.75 W/W) 8-32
Table 8-10 Mechanical Batch Mixing Operations (Tar Sand No. 8 Range of Conditions: 3-8 Minutes Mixing; 65-140 Wt % Total Water; 70°F Temperature. Product Screened from Sand Using 20 Mesh Sieve in an ASTM Shaker) 8-34
Table 8-11 Sand Reduction Experiments with Continuous Screw (Feed Rate : 30 lb/hr Tar Sands and 25 lb/hr of Water) 8-34
Figure 8-19 Continuous Screw and Rotary Screen 8-35
Figure 8-20 "Good" Mixers for Agglomeration 8-37
Table 8-12 Process Comparison on Good Quality Oil Sands Area B : 10-7 Grade 8-39

Table 8-12 Process Comparison on Good Quality Oil Sands Area B : 10-7 Grade 8-39
Table 8-13 Sand Reduction of Marginal Quality Oil Sands for Low Water Content Agglomerates 8-40
Figure 8-21 Coking 8-40
Table 8-14 Comparison of Heat Requirements for Direct Fluid Coking of Feed and Pruducts 8-41

9 SOLVENT DILUTION

Figure 9-1 Problem of Dilution and Settling as a Froth Upgrading Process . . . 9-2
Figure 9-2 Comparison of Viscosity-Temperature Relationships of Oil and Various Solvents 9-4
Table 9-1 Inspection on Solvents and Solvent Mixtures 9-5
Figure 9-3 Viscosities of Oil-Solvent Mixtures 9-6
Figure 9-4 Viscosity-Temperature Relationship for Solvent Dilution of Oil Showing Vapour Pressure Limitations 9-7
Figure 9-5 Solution Rates of Beaver River Oil & Treatment of Solution Rate Data 9-9
Table 9-2 Solution Rate Data 9-10
Figure 9-6 Effect of Solvent Power and Viscosity on Solution Rate of Oil at 140°F 9-11
Figure 9-7 Effect of Solvent Viscosity on Sludge Formation Tendency in Oil-Solvent Mixing at 140 °F 9-12
Table 9-3 Froth Upgrading Techniques Studied 9-14
Figure 9-8 Froth Upgrading Techniques Studies (Shown as Relative Volume for Upgrading Beaver Creek Froth at 150 °F) 9-15
Figure 9-9 Effect of Chemical Additives on Heavy Minerals and Solids in Froth . 9-17
Table 9-4 Effect of Inorganic Additives on Solids Removal from Froth Separated with Aeration 9-18
Table 9-5 Effect of Organic Additives on Solids Removal from Froth Separated without Aeration 9-20
Figure 9-10 Oil Recovery Decreases with Solvent to Oil Ratio 9-23
Figure 9-11 Water Content of Total Oil Phase Decreases with Solvent to Oil Ratio and Oil Loss to Water and Solids Increases 9-24
Table 9-6 Membranes 9-28
Figure 9-12 Preliminary Data on Solids Removal and Contaminants in Oil Phase vs Centrifugal Force 9-30
Table 9-7 Comparison of Methods of Oil -Water Interfacial Agitation (3 Hours Operation at 165 °F , 1:1 Good Quality Beaver River Froth to Toluente Wt Ratio) 9-32
Figure 9-13 Effect of Time on Separation of Water-Wet Solids from Froth with Different Chemical Additives 9-33
Figure 9-14 Solids Separation Independant of Temperature 9-36
Figure 9-15 Effect of Sodium Carbonate and Silicate Addition on Water-Wet Solids Removal from Good Quality Froth by Solvent Dilution (Standardized Conditions) 9-38
Figure 9-16 Preliminary Data on the Effect of pH on Water-Wet Solids Removal from Good Quality Froth 9-39
Figure 9-17 Effect of Sodium Phosphates Concentration and Froth Types, on Water-Wet Solids Removal 9-41
Figure 9-18 Flow Plan Combination Settling - Centrifuging Process 9-43
Table 9-8 Conditions and Results Projected for Upgrading Beaver River Froths in a Continuous Solvent-Dilution Process 9-44

III. MECHANISMS

10 INTERFACIAL

Table 10-1 Surface Chemistry 10-2
Figure 10-1 Surface Tension of Mildred Lake Oil 10-4
Figure 10-2 Interfacial Tension of Oil 10-5
Figure 10-3 Effect of pH on Interficial Tension and Contact Angle 10-7
Figure 10-3 (b) Oil Globule Behaviour (@9 pH) 10-8
Figure 10-4 Surface Tension of Water in Contact with Oil and Work of Adhesion of Oil and Water 10-9
Table 10-2 Summary of Interfacial Properties 10-10
Figure 10-5 Adhesion Tension of Solids/Oil Interfaces 10-12
Figure 10-6 Adhesion Tension of 325 - Fines Against Oil Settling Volumes . . 10-13
Figure 10-7 Solids in Tar Sands Are Already Water Wet 10-15
Figure 10-8 Zeta Potential of Benzene Extracted Oil Versus pH 10-19
Figure 10-9 Zeta Potential vs pH Relation for (m) Mineral Suspensions . . . 10-20
Figure 10-10 Zeta Potential and pH Data for "Clay" Samples 10-22
Figure 10-11 Cation & Anion Effect of Chloride Salts on Zeta Potential of a Clay Suspension 10-24
Figure 10-12 Zeta Potential Relationsip of Pilot Plant Feeds 10-26

11 MICROSTRUCTURE

Figurell-1 Schematic Crossectional Representation of the Structure of Tar Sand (Particles are Negatively Charged) 11-3
Table 11-1 Possible Oxidation Reactions 11-5
Table 11-2 Possible Acid Reactions 11-5
Table 11-3 Mechanism of Oxidation 11-5
Table 11-4 Low Oil Sand Grades Partially Oxidized during Original Formation . 11-6
Table 11-5 Soluble Salt Content of Tar Sands 11-6
Table 11-6 Carbonates - Heavy Minerals Cause Alkaline pH Natural Oil Sands pH 6.5 - 8.5 11-7
Table 11-7 Heavy Minerals (1% 2.96 g/ml) 11-7

12 SEPARATIONS SUMMARY

Figure 12-1 Tar Sand Hot Water Flotation Process 12-2
Table 12-1 Factors Influencing Flotation 12-4
Figure 12-2 Slurrying Tar Sands with Water (Laboratory "Batch" for Time T) . . 12-5
Figure 12-3 Oil Sand Behaviour Relationships 12-7
Figurel2-4 Bitumen Particles 12-8
Table 12-2 Some Simplified pH Conditioning Reactions 12-9
Figurel2-5 Bitumen Flotation 12-10
Figurel2-6 Air Attachment Mechanism 12-11
Table 12-3 Low Grades More Difficult to Separate Efficiently 12-13
Table 12-4 Treating Low Grade Tar Sands 12-13
Figure 12-7 More Contaminant Removal Needed with Poorer Oil Sands 12-15

IV. CONCLUSION

V. APPENDICES

V1 HOT WATER FLOTATION PARAMETERS

V1-Table 1 Studies on the Effects of Water in Mixing, Mixing Intensity and Mixing Time with a "HighWater" Area B Tar Sand 1-3
V1-Table 2 Effect of Low Addition in Mixing with and without Air in Subsequent Separation Aged, Area B Tar Sand 1-4
V1-Table 3 Studies on the Effects of Water in Mixing, Mixing Intensity and Mixing Time with an Area D Tar Sand 1-5
V1-Table 4 Effect of Low Water Additions in Mixing on an Area D, Hole 4, Tar Sand with and without Air in Subsequent Separation 1-6
V1-Table 5 Effect of Minimum Slurry(1)and Standard Water Additions in Mixing on Fresh Spot Samples of Area B, and Area D, Hole 9 and 11 Tar Sands 1-7
V1-Table 6 Effect of Aeration Time, Rate, Frequency, Water Addition, and Tar Sand Charge with an Area D, Hole 10 Tar Sand 1-8
V1-Table 7 Cold Slurrying Tar Sands with Water prior to Dense Phase Separation Gave Higher Oil Recoveries and Cleaner Sand 1-9
V1-Table 8 Effect of Air Rate on Oil Recovery and Froth Composition for a Good Quality Tar Sand - Area B 1-10
V1-Table 9 Effect of Air Rate on Oil Recovery and Froth Composition for a Poor Quality Tar Sand - Area D, Hole 11 1-11
V1-Table 10 Effect of Air Rate on Oil Recovery and Froth Composition for a Poor Quality Tar Sand - Area 4 1-12
V1-Table 11 Effect of Air Rate on Oil Recovery and Froth Composition for a Poor Quality Tar Sand - Area D, Hole 9 1-13
V1-Table 12 Effect of Air Rate with Fresh Spot Samples of Area B, Area D Holes 9, and 11, Tar Sands 1-14
V1-Table 13 Effect of Temperature with a "High Water" Area B Tar Sands 1-15
V1-Table 14 Effect of Temperature with a New Area 4 Tar Sands 1-16
V1-Table 15 Area D Tar Sand Sample From Cut Adjacent to Hole 9 Contained Two Types of Tar Sands Separable by Dry Sieving 1-17
V1-Table 16 Effect of Temperature with an Area D, Hole 11, Tar Sands 1-18
V1-Table 17 Effect of Tar Sand "pH" on Processability 1-19

V2 INORGANIC ADDITIVES IN SLURRYING

V2-Table 1 Effect of Sodium Salt Concentration on Processability of a Poor Quality Tar Sand (Hole 21A Tar Sand Containing 5.4 % Oil, 7.2 % Water, 31.5 % 200-Fines, 55.9 % Sand) 1-3
V2-Table 2 Effect of Phosphate Type and Concentration on Separation of an Aged(1) Tar Sands Dug from a Surface Hole(2) 1-4
V2-Table 3 Effect of Phosphate Type and Concentration on Separation of an Aged(1) Tar Sands Dug from a Surface Hole(2) 1-5
V2-Table 4 Effect of Sodium Salts and pH on Various Tar Sands 1-6
V2-Table 5 Chemical Adjusted Processability of Beaver River Tar Sands 1-7
V2-Table 6 Chemical Adjusted Processability of Beaver River Tar Sands 1-8
V2-Table 7 Chemical Adjusted Processability of Beaver River Tar Sands 1-9

V2-Table 8 Chemical Adjusted Processability of Beaver River Tar Sands 1-10
V2-Table 9 Chemical Adjusted Processability of Beaver River Tar Sands 1-11

V3 ORGANIC ADDITIVES IN SLURRYING

V3-Table 1 pH (Sodium Hydroxide) and Anion (Oxalate) Effects in Separation (Hole 11 Tar Sand and Nitrogen in Aeration) 1-3
V3-Table 2 Effect of Oxalate on Separation (Hole 11 Tar Sand and Nitrogen in Aeration) 1-4
V3-Table 3 Effect of Pyridine and Stannous Chloride on Separation (Hole 11 Tar Sands and Nitrogen in Aeration) 1-5
V3-Table 4 Exploratory Experiments with Additives and Different Tar Sands (Nitrogen in Aeration) 1-6
V3-Table 5 Effect of Addition of Solutions of Additives of Different pH (Hole 11 Tar Sand Containing 7.8 % Oil, 4.1% Water, 15.3% Fines(200-) and 72.8% Sand) 1-7
V3-Table 6 Effect of Addition of Sodium Salt Solutions in Mixing of Different pH, but Equivalent Na Content (Hole 11 Tar Sand Containing 10.8 % Oil, 2.1% Water, 7.1% Fines (200-) and 80.0% Sand) 1-8
V3-Table 7 Effect of Addition of Sodium Salt Solutions in Mixing of Different pH, but Same Na Content (Hole 11 Tar Sand Containing 10.8 % Oil, 2.1% Water, 7.1% Fines (200-) and 80.0% Sand) 1-9
V3-Table 8 Effect of Surfactants Class with pH Control on a Hole 11 Tar Sand . 1-10
V3-Table 9 Effect of Nonionics and Silicones of Different Molecular Weights on Area B and Hole 11 (with pH Control Tar Sand 1-11
V3-Table 10 Effect of Amphoteric Surfactants with pH Control on a very Low Oil-High Fines Hole 21A and High Oil Hole 11 1-12
V3-Table 11 Effect of HLB Surfactants with Area B and Hole 11 Tar Sand . . . 1-13
V3-Table 12 Effect of HLB Surfactants with pH Control and a Hole 11 Tar Sand . 1-14
V3-Table 13 Complexing Chemical Addition to Beaver River Tar Sands 1-15
V3-Table 14 Complexing Chemical Addition to Beaver River Tar Sands 1-16
V3-Table 15 Complexing Chemical Addition to Beaver River Tar Sands 1-17

V4 SAND REDUCTION SEPARATIONS

V4-Table 1 Effect of Water Addition (or Shear) on Sand Reduction in Mixing . . 1-3
V4-Table 2 Effect of Water Addition (or Shear) on Sand Reduction in Mixing . . 1-4
V4-Table 3 Effect of Water Addition (or Shear) and Temperature on Sand Reduction in Mixing 1-5
V4-Table 4 Effect of Water Addition (or Shear) and Temperature on Sand Reduction in Mixing 1-6
V4-Table 5 Effect of Water Addition (or Shear) on Sand Reduction in Mixing . . 1-7
V4-Table 6 Effect of Temperature on Sand Reduction by Shear Only 1-8
V4-Table 7 Effect of "Clay" on Sand Reduction (Mortar and Pestle Experiments) (Tar Sand, No. 11, Contained 15 Wt % Oil and 6 Wt % Water) . . . 1-9
V4-Table 8 Effect of Addition of Water and Fluid Coke on Sand Reduction in Mixing(3) (Mortar and Pestle Experiments) (Tar Sand, No. 2A, contained 13 Wt % Oil and 7 Wt % Water 1-10
V4-Table 9 Effect of Addition of Water and Fluid Coke, and Temperature on Sand Reduction in Mixing(3) (Motar and Pestle Experiments) (Tar Sand, No. 3, contained 2 wt % Water and 18 wt % Oil) 1-11
V4-Table 10 Mechanical(1) Batch Mixing Operations (Tar Sand, No. 8 contained 5 wt % water and 15 wt % Oil Average results for condition: 65 and 110 wt % water,70°F, 3 1/2 and 7 1/2 min mixing time) 1-12
V4-Table 11 Summary of Experimental Results with Continuous Helix 1-13

V5 SOLVENT DILUTION CLEAN UP OF OIL

V5-Table 1 Effect of Temperature, pH, and Sodium Salts on Water-Wet Solids Removal from Good Quality Froth by Solvent Dilution with 1:1 Xylene Wt. Ratio (Froth Composition wt %: Water -23, Solids -5, and Oil -72) . . . 1-3
V5-Table 2 Calibration of Apparatus in terms of Rate of Water-Wet Solids Separation as a Function of Particle Size (6 % Solid Spheres in a 1:1 Oil-Xylene Phase) . . . 1-4
V5-Table 3 Effect of Sodium Tripolyphosphate on Other Types and Quality Beaver River Froths . . . 1-5
V5-Table 4 Effect of Buffer solutions in Mixing and Separation of Water-Wet Solids from Beaver River Froth - Run #109 (Froth Composition, wt %: Water -18; Solids -8; and Oil -74) . . . 1-6
V5-Table 5 Miscellaneous Process Effects Studied as a Function of Solids Removal from Good Quality Beaver River Froth at Standard Conditions (Froth Composition Wt % : Water -16; Solids -6; and Oil -78) . 1-7
V5-Table 6 Effect of Mixing on Water-Wet Solids Removal from Beaver River Froth-Run #109 "Standardized Conditions Were Not Optimum" (Froth Composition Wt %: Water -18; Solids -8; and Oil -74) . . . 1-8

V6 EXPERIMENTAL TECHNIQUES AND EQUIPMENT

V6-Figure 1 Apparatus for Determining the Composition of Mixtures of Solids-Oil-Water . . . 1-3
V6-Figure 2 Brass Pot Extraction Apparatus . . . 1-5
V6-Figure 3 Some Typical Temperature Profiles Measured with a Recorder . . . 1-6
V6-Figure 4 Laboratory Brass Pot Tar Sand Extraction Equipment . . . 1-7
V6-Table 1 Laboratory Tar Sand Extraction Equipment . . . 1-8
V6-Table 2 A Modified Pot Extraction Procedure for Laboratory Tar Sand Separations . . . 1-10
V6-Table 2a A Modified Pot Extraction Procedure for Laboratory Tar Sand Separations . . . 1-11
V6-Table 3 Data Summary and Weight Balance Calculations (100 g Tar Sand Charge) . . . 1-12
V6-Table 4 Reproducibility and Temperature Studies (Brass Pot) with a Sample (#1) of Homogenized Bench Unit Tar Sands Feed . . . 1-13
V6-Figure 5 Zeta-Meter . . . 1-16
V6-Figure 6 Concept of the Zeta Potential . . . 1-17
V6-Figure 7 Effect of Ionic Strength on Thickness of Diffuse Layer . . . 1-18
V6-Figure 8 Electrophoretic Cell . . . 1-20
V6-Table 5 Surface Tension Measurements(1) . . . 1-22
V6-Figure 9 Surface Tension Versus Temperature Correlation for Liquids Used in Instrument Calibration (Literature Values Mostly from Handbook of Chemistry and Physics) . . . 1-23
V6-Figure 10 Literature Versus Measured Surface Tensions (Symbols and Data - See Table 6. High Temperature, °F, Measurements Shown Numerically) . . . 1-24
V6-Table 6 Interfacial Tension Measurements(1) . . . 1-25
V6-Figure 11 Literature Versus Measured Interfacial Tensions (Symbols and Data - See Table 1) . . . 1-26
V6-Figure 12 Comparison of Literature and Experimental Measurements of Interfacial Tension (Dynes per cm) . . . 1-27
V6-Figure 13 Preliminary Comparison of Interfacial Tension as Measured by the Ring Method and the Pendant Drop . . . 1-28
V6-Figure 14 Infra-red Adsorption Spectra of Saturates Separated from Hole 11 Tar Sand by S.A.R.A with Solvent Recycle . . . 1-30
V6-Figure 15 Infra-red Adsorption Spectra of Aromatics Separated from Hole 11 Tar Sand by S.A.R.A with Solvent Recycle . . . 1-31

V6-Figure 16 Infra-red Adsorption Spectra of Resins Separated from Hole 11 Tar Sand by S.A.R.A with Solvent Recycle 1-32
V6-Figure 17 Infra-red Adsorption Spectra of Asphaltenes Separated from Hole 11 Tar Sand by S.A.R.A with Solvent Recycle 1-33
V6-Figure 18 Infra-red Adsorption spectra of Acetone Extract from Solids after Removal of Benzene Soluble Oil 1-34
V6-Figure 19 Infra-red Spectra of an Ethanol Extract of Hole 11 Tar Sands 1-35
V6-Figure 20 Infra-red Adsorption Spectra of Surfactant Film which Peeled off from Oil Droplet under Water 1-36

V7 ORIGINAL BEAKER FLOTATION EXPERIMENTS

V7-Table 1 Beaker Procedure 1-2
V7-Table 2 Preliminary Laboratory Extraction Comparison Using Good Quality Tar Sand 1-4
V7-Table 3 Preliminary Laboratory Extraction Comparison Using an Augered Undisturbed Tar Sand from Location "D" 1-5
V7-Table 4 Laboratory Extraction Comparison Using Augered "Disturbed" Tar Sands from Location D 1-6
V7-Table 5 Final Test of Laboratory Extraction Method Run Under Comparable Conditions(1) 1-7
V7-Table 6 Laboratory Extraction Comparison Between Operators on Different Tar Sands 1-8
V7-Figure 1 A Preliminary Correlation of Oil Recovery and Total Suspended Solids in the Water Phase 1-9

V8 SOLVENT EXTRACTION

V8-Figure 1 Apparatus Used in Applying Voltage 1-2
V8-Figure 2 Appendix D Figure 5 Voltage-Current Relation for System 1-2
V8-Table 1 Some Experiments on the Effect of Electrostatic De-emulsification of Froth with and without Solvent Dilution 1-4
V8-Table 2 Some Experiments on the Effect of Electro-Separation of Tar Sands (Tar Sand was Premixed at 140-150 °F with 31-39 Varsol in a Motar with a Pestle for 5 minutes and transfered to the apparatus shown in Figure 1, which was maintained at about the same temperature . . . 1-5
V8-Figure 3 Diagrammatic Representation of Systems Studied 1-6
V8-Figure 4 Volume Ratio of Total Oil to Water in the System Showed a General Relation with Voltage 1-7
V8-Figure 5 A Laboratory Dilution - Settling Apparatus 1-9
V8-Figure 6 Small Scale Dilution Settling Apparatus 1-10

PREFACE

Many fundamental and small scale studies directed at a better understanding of the nature and behaviour of oil sands were carried out at the Imperial Research Department in Sarnia over the period from 1957 to 1966. The purpose of this report is to summarize these past investigations that may be of some value to researchers who have been attracted to the field by the recent surge of interest in oil sands as a much needed Canadian energy resource for development.

In these past studies, carried out both in micro and small bench scale experiments, many different oil sands samples were examined for composition and structure, component types and properties, as well as mechanisms of behaviour both on exposure and in separation. Composition of mined oil sands was defined based on laboratory separations in terms of the main components of oil, water, different mineral types, and gas. Oil sands was therefore found to be a multi-phase complex system of components that varies significantly in composition.

The effects of character and interfacial relationships of these components on the behaviour of oil sands in separation shows that there are several important physical-chemical-electrical properties in phase separation. For example, maximum efficiency of separation is achieved at slightly alkaline pH which corresponds to maximum charging of interfaces as measured by zeta potential. These phase relation studies not only provide some data on properties and behaviour, but also give insights on why certain oil sands separate well while other oil sands behave poorly. The structure and mechanisms of behaviour of oils sands is developed based on a number of small scale laboratory experiments.

The ideas, speculations, notes, and conclusions that have been retrieved from memos and reports from this period of oil sands research, are preserved in this organization of data for easy access by the reader to a specific area of interest.

J. A. Bichard

ii

DESCRIPTION OF CONTENTS

The composition and components of the oil sands, performance in separation processes, and mechanisms of behaviour are described in the three main sections of this report. These studies carried out in 1957 to 1966, present an overview of the problems of separation with some solutions for more efficient oil recoveries, especially from lower grades of mined oil sands.

I. COMPOSITION

1. Oil Sands

The several components and variations in composition of oil sands are briefly described. A generalized relationship of increasing fines content with decreasing oil content, that define the different grades of mined oil sands used in these studies is developed. This basic relationship is the main correlating parameter with processability of oil sand in water separation processes. Oil sands are differentiated on the basis of sample location in the formation and not on geological facies or lithology, although there is a general relationship.

2. Oil

The physical and chemical properties of the oil as well as those of its components are summarized as a function of variations in oil quality that occur in the formation. Greater emphasis is placed on the behaviour of interfacially active polar components that play a key role in oil sand separations. Aqueous soluble oil is shown to be amphoteric in behaviour as a function of pH.

Oil solubilities in different organic solvents are defined for use in solvent extraction. A new solvent solubility parameter is derived, and an internal structure of an oil particle is proposed from these experimental observations.

3. Minerals

In general, essentially the same mineral types are found, except in different amounts and size distributions, in all of the oil sand samples studied. These samples were obtained from different locations and depths over an area of a few square miles near Mildred and Beaver Lakes.

As sand (70-88% of 325 mesh) is relatively inert and readily separates in water, it was only briefly examined. Fines (1-30% of 325 mesh) is found to be a weathered mixture of kaolin and illite clay minerals, with some fine silica. Fines occur mostly in interbedding strata and small lenses in the lower grade oil sands. Smaller particles (5µ) are predominantly clay minerals. Water phases also contain colloidal (0.5µ) organic-clay-inorganic suspensions, that are very stable in slightly alkaline aqueous media.

Most of the small amount (1%) of heavy (2.96 g/ml) minerals are inert. However, as (1) heavy minerals tend to concentrate more than other minerals in the oil froth in hot water flotation, and (2) some sulphides and carbonates occur that are potentially reactive, then a more extensive examination of these mineral types was carried out and details are recorded.

Oxidation of sulphides by air is slow and can occur in the mined oil sands by air replacement of water lost by evaporation. The acid (e.g. H_2SO_4) generated decreases the natural 7-8 pH established by reaction of solids e.g. (carbonates) with water. Under acid conditions, carbonates as well as other minerals are relatively more soluble resulting in significant amounts of polyvalent ions (e.g. Ca^{++}, Fe^{++}) in solution. These ions can migrate in the water films and be deposited on surfaces in higher pH zones of the microstructure.

Significant mineral contamination with iron is observed especially on the surfaces of smaller particles encountered in lower grades of oil sands. This and other evidence indicate that in general lower grade oil sands have undergone some oxidation probably at the time of the formation of the oil sands. Since then these microstructures have attained equilibrium, but these effects are still contributing factors to poor processability of lower grade oil sands.

4. Water

Sodium predominates with some magnesium and calcium cations in most separated water phases after contact with oil sands. Colloidal precipitates of silica, alumina and iron, probably hydroxides associated with polar components from the bitumen also occur together with suspensions of clays from alkaline oil sands. This Fe/Al/Si complex chemical system may be a bridging agent that adversely affects processability.

Relationship of pH, specific conductance, and zeta-potential of suspended clays in the water phases from hot water separations of different grades of oil sand treated with different inorganic additives are developed. These relationships reflect changes in processability in the hot water flotation separation process.

5. Gas

Methane, carbon dioxide and nitrogen are the main gases present in the oil sands samples studied, other than air from exposure in sampling. Evacuation experiments of freshly cut cubes of oil sand under water indicate that nitrogen and carbon dioxide occur in either unsaturated voids between the mineral grains, or dissolved in the water films on the solids. Nitrogen alone may indicate that oxidation has taken place. Whereas, a small amount of methane and some CO_2 are dissolved in the oil phase, as observed by substantial oil filming in the surrounding water phase on completion of evacuation, when methane was mostly recovered. Dissolved gases, although a very minor component, can be a factor in flotation of bitumen in the hot water process.

II. BEHAVIOUR

6. Flotation

Several oil sand grade effects, such as high fines (clays), blended grades, and calcium salt additions, in a two-stage process of primary (no-aeration) and secondary (aeration) separation used in most of the laboratory separations are explored. Also data on many of the main hot water flotation process variables, such as degree of mixing, slurry water, pH, temperature, aeration with multiple skimmings for high oil recoveries, are evaluated.

Further, separation effects in the more optimum pH range of 7-10 for highest oil recoveries with selective additives to control the deleterious effects of polyvalent ions and high fines (clays) are also investigated. Sodium tripolyphosphate and sodium silicate were found to be most effective in achieving high oil recovery with lower grades of oil sands.

7. Additives

Oil recoveries are maximized when carried out at optimum pH of ~9 depending on the ionic strength of the water phase. However, although slightly alkaline pH by the addition of sodium hydroxide is the prime condition for high oil recoveries as well as lower contamination of oil froth with solids and water, the anion of the sodium additive can also play a significant role. This is particularly important in processing lower grades of oil sands. Although more expensive, sodium silicate gives a more stable and better separation even in admixture with sodium hydroxide. Sodium tripolyphosphate is most effective in counteracting the effect of polyvalent ions (or "polyvalent ion exchanged" clays) that cannot be controlled by sodium hydroxide. Maximum oil recoveries are achieved at optimum concentrations of additives.

Small quantities of specific organic additives together with inorganic conditioning agents can also effect additional improvements in froth quality and in oil recovery from lower grade oil sands. These additives adjust the amount of naturally polar components to an optimum concentration for maximizing oil recovery.

8. Sand Reduction

A novel oil sand separation process called "Sand Reduction" was developed, but has not been applied commercially. In the process, oil sand is mixed with cold (70°F) water (80%) that results in separation of clean sand (75%). The oil with some solids and water form oil agglomerates that can be separated and either fed directly to coking or processed further for removal of solids and water contaminants by solvent dilution.

Sand Reduction is a more energy efficient process than Hot Water Flotation and hence is more economical. Further, it uses less water that can be recycled. It has the flexibility to be used at the mining site reducing conveyance of oil sand to a fixed separation plant, as well as process water and solids to disposal.

The process was initially developed without the use of additives, and with tar sands that had aged. Subsequent laboratory studies showed that with inorganic conditioning reagents and agglomeration aids, lower grade oil sands can give acceptably high (90%) oil recoveries. The process was demonstrated in small scale continuous pilot plants on both aged and fresh oil sands on-site at Sarnia, Ontario and Mildred Lake, Alberta.

9. Solvent Dilution

Centrifuging, ultrasonics, and mechanical separation techniques are evaluated for froth and agglomerate cleanup. Centrifuging was found to be the best separation method to overcome emulsion problems and achieve high oil recoveries.

Studies were carried out in an attempt to define a solvent dilution gravity settling, separation process. The main problem identified is the accumulation of skins of surfactants - solids at the oil/solvent-water interface that restricts the passage of water-wet solids. On breakthrough of the oil/water interface with water wet separating sand, appreciable oil/solvent is occluded resulting in high oil/solvent losses in the wet sand.

A vibrating screen at the interface is a potentially effective method for breaking up the interfacial skins and allowing free passage of water-wet clean solids. This technique indicates the possibility of developing a gravity settling process to recover the bulk (<90%) of contaminant free (>2% solids) oil/solvent overhead, and a clean water-wet solid discard underflow, using mechanical agitation of the oil/water interface to effect clean separation. Any build up of interfacial emulsion is removed and separated by centrifuging with appropriate additives for high oil and solvent recoveries. Hence, substantial reduction in size and expense of centrifuging may be achieved.

III. MECHANISMS

10. Interfacial

Surface and interfacial tensions as well as contact angles of oil on silica as functions of pH and temperature are used, together with settling volumes of fines for measuring oil-sands wettability, to determine the most probable relationships of the component particles in the microstructure of oil sands. These data support the theory that essentially most if not all the solids in the formation are water-wet. This is the basis for all oil sands-water separation processes. Further, air occlusion in oil during proper conditioning is essential in attaining high oil recoveries in primary hot water flotation.

Zeta potential (surface charge) measurements on suspended oil and solid particles in water are negative, except in the present of (adsorbed) polyvalent ions (e.g. Fe^{+++}) that can act as a bridging agent for oil-solids attachment. Particle surface charge is also decreased at different rates with increasing solution concentrations of both anions and cations, especially polyvalent cations. The role of pH adjustment is essentially to ionize the carboxylate surfactants that make the hot water flotation separation process possible. Hence, salt effects, both connate and added, can lower surface charge that result in oil-solids association and thus substantially reduce oil recovery. The properties of the water phase are clearly shown as an essential control of separation performance.

11. Microstructure

An oil sand microstructure in which water-wet touching solids create three-dimensional water film capiliaries that transverse the oil sand system on the surfaces of solid particles is proposed.

The oil in high grade oil sands of >10% oil content is also in a partially continuous phase of tortuous oil threads in the interstices between the water-wet solids making the normally unconsolidated solids system cohesive. Hence work (mixing energy) has to be expended to overcome the cohesion energy of the oil to break the threads apart into smaller oil particles in mixing with water. On the other hand, the oil in lower grade oil sands of<10% oil content is in the form of smaller oil particles (flecks) in the interstices between the solids. This structure is more friable and immediately breaks down in mixing with water.

This concept implies that the separation of oil from minerals by water is already essentially complete in the microstructure of the natural formation. Hence, any oil sand-water separation process, such as "Hot Water Flotation" or "Sand Reduction" is more a method of physically separating water-wet solids and efficiently collecting the bulk of oil with some entrained solids and water. Different oil sands require different energy inputs for optimized results.

A mechanism of oil sand "aging"is also presented.

12. Separations

In general, water separation techniques can be made to perform well on high grade oil sands that will constitute the main part of a selected mining area. Hence demonstrations of high oil recovery with only these types of oil sands are unrealistic measures of overall processing efficiencies, unless modifications can be applied to handle low grades of oil sands.

As most mining areas will contain significant amounts of low grade oil sands of 6-10%, the ability of a water separation technique to attain high (90+%) oil recoveries and good oil product qualities with those low grades is a crucial technical problem that can have economic impact on the life of a commercial venture.

The major problem of separating lower grade oil sands is not only one of fines or clays, but rather the extent of "oxidation" that took place at the time of the deposit, salt content, and colloidal material that can affect bitumen flotability. As such, it is necessary to recognize what is the specific oil sand "state" to be separated and what is the best type of solution to achieve the most efficient (cost effective) separation.

The proposed practical solution to the problem is to measure specific properties of the oil sand feed to the process for use in selecting suitable bulk chemical additives that when balanced with mechanical energy input in mixing can modify the surfaces of the separating phases for maximum oil recovery in separation.

The several mechanisms involved in the "Hot Water Flotation" process are examined and compared briefly with those of Sand Reduction, with emphasis on processability of lower grade oil sands.

I. COMPOSITION

1

OIL SANDS

The Alberta Oil Sands[1] is one of the world's largest known oil reserves. The origin, the extent of the occurrence and the potential bitumen production of the tar sands has still to be resolved. The Alberta Oil and Gas Conservation Board has estimated the total oil reserve[2] at over 800 billion barrels in place, of which ~80% occurs in the Athabasca deposit that extends over ~6 million acres adjacent to the Athabasca River. This deposit is covered with overburden varying up to ~2,000 feet. However, some exposed outcroppings occur along the Athabasca River over a distance of about 60 miles, see Figure 3-5. These oil sand outcroppings vary in depth to about 200 feet and the overburden up to about 250 feet.

It is, therefore, consistent with the general modes of occurrence that two basically different approaches are being considered for the production of oil. First, mining of the tar sands, bitumen separation and upgrading to obtain a synthetic crude, is being actively developed in locations where there are outcroppings of good grade oil sands and low overburden. Second, in-situ recovery of the oil is a logical future development needed for the bulk of the tar sands with large overburden.

The studies reported here are concerned with the mining separation approach. Most of the oil sand samples used were obtained from the Mildred Beaver Lake area, Figure 3-5. The immensity of the deposit, however, clearly implies that the generalizations and speculations made within the context of these limited studies do not necessarily apply to all oil sands.

1-1 Components

The composition of oil sands is generally reported in the literature as a mixture of four main components, i.e. oil, water, fines and sand. The distinction between sand and fines is made according to particle size. Material passing through a 325 U.S. (<44 μ) mesh seive is reffered to as fines which includes silt, very fine quartz, and clay minerals. Another component of the solids is heavy (>2.96 g/ml) minerals that occurs in small (<1%) amounts.

---

[1] *Either Oil Sands or Tar Sands; as well as either oil or bitumen or tar; are used in this report as equivalent terms.*

[2] *Includes the Athabasca, the Bluesky-Gething and the Grand Rapids Deposits*

In addition to the four main components used most frequently to define oil sands, as well as heavy minerals that was found to be a unique feature of the solids, there are surface active organic polar compounds, colloids, and ions in the water phase, and a small amount of gas in the natural structure. A more detailed classification of components is given in Table 1-1. These components form a multi-phase complex system of several constituents in varying proportions involving interfacial and colloidal phenomena in the micro structure of the oil sand.

As oil is the main component of commercial interest, the general composition of oil sands is plotted[3] as a function of this component in Figure 1-2. Oil sand grades of less than 6% oil are probably uneconomic to process and are rejected with the overburden. Hence, a future commercial separation process will mine oil sand grades of 6 to 18% oil for extraction of bitumen. An average oil content is 10-12%. Higher grades separate easily, while lower grades separate poorly in the hot water flotation process.

The first obvious component difference in Figure 1-1 is that low grade oil sands contain appreciable amounts of fines that are mostly clay minerals. However, the behaviour of "clay" in separation is variable, in that some "clay" appears to have only a small effect, while other "clay" has a drastic effect. The cause of variability in separation is thus more subtle than just either fines, clay, minerals or grade. Hence, a better understanding of separation processes became a main objective of the research recorded in this report.

As different types of oil sands occur, a particular separation process must have flexibility to handle these variations. Thus it is important to know how these variations, both in composition, in quality and in structure, affect the separation process so that optimization may be achieved.

1-2 Compositions

Inspections on twelve tar sand samples (average of 2.0 g/cc or 125 lbs/sq ft) used in an oil sand characterization study are shown in Table 1-2. The oil, generally referred to as benzene or toluene soluble material, varied between 5-13 wt%,for an average grade of 9.4% bitumen. Highly polar hydrocarbons not extracted with toluene, but soluble in polar solvents such as acetone and particularly pyridine were about 1-2 wt% on the total oil. The water varied from 4-11 wt% on oil sands. Fines (~2.2 g/cc) were 5-34 wt%, and sand (~2.65g/cc) 54-77 wt%. With the exception of one value of 0.1 wt% iron, the remaining eleven tar sands exhibited iron contents between 0.5-0.8 wt%. pH varied from 4.3-8.3. The heavy mineral content (2.9 g/cc) of the total solids ranged from 0.2-1.0 wt%, and appeared to decrease with depth. The oil content that has been observed to generally increase with depth at the river outcroppings near Mildred Lake is not shown too clearly by these data.

The compositions of this small selected group of oil sands samples are plotted in Figure 1-2 as a function of fines content to illustrate the variability of oil sands within the general correlating pattern. As the clay lenses have a higher ability to retain water, then this is reflected in the general correlation. The scatter in fines data is because lower grade oil sands occur often with "clay" strata or lenses in between layers of oil sands from the deltaic deposition of the formation. An example is shown in Table 1-3 for the highest clay content oil sands. Initially, after extraction of oil, the fines content was 1% by dry screening of the total solids. However, after dispersing and water wetting, mainly the 10+ mesh, a 35% fines content resulted. Most of the fines therefore occurred in the original oil sand as small "chopped up" lumps of "clay" lenses from homogenizing the samples. However, other samples here show fines to be dispersed in the oil sand structure.

---

[3] *Liquid correlations are least square lines through 100 data points. The fines content is based on less data, and scatter is greater due to the arbitrary inclusion of "clay" lenses in sampling (see Table 1-3).*

Table 1-1

The Components of the Tar Sands

Oil	• (1) Definition of total oil: a visco-plastic hydrocarbon containing saturates, aromatics, resins (polar compounds), and asphaltene type components. • (2) Working† definition of oil: a benzene or toluene soluble portion of the tar sands. • (3) Polar hydrocarbons (a) soluble in polar solvents (b) soluble in aqueous solutions (c) present at the interface in contact with aqueous media.
Solids	• (1) Working† definition according to size (defined) (a) Sand - 325+ mesh material (+44μ material) (b) Silt - 325 mesh to 5μ (2-44μ material) (c) Clay - 5μ and 0.5μ (2μ and less material) (d) Colloid - less than 0.5μ (10-5000A material) • (2) According to chemical composition (a) Silica (α quartz) (b) Heavy minerals (c) Clay minerals, e.g. illite, kaolinite (d) Carbonaceous fragments
Water	• (1) Hydration (a) Lattice (b) Surface film • (2) Unbonded (a) Free film (b) Formation free and trapped • (3) Conate water† includes unbonded water and surface hydration as determined by soxhlet extraction. • (4) Total water includes connate plus lattice water as determined by ash analysis.
Salts and Ions	• (1) Salts insolubles in aqueous media. • (2) Salts soluble in aqueous media. • (3) Surface adsorbed ions. • (4) Ions in aqueous media.
Gas	• (1) Dissolved in oil phase. • (2) Dissolved in aqueous phase. • (3) Free in the structure.

† Convenient for laboratory operations.

Figure 1-1

Oil Sands Composition

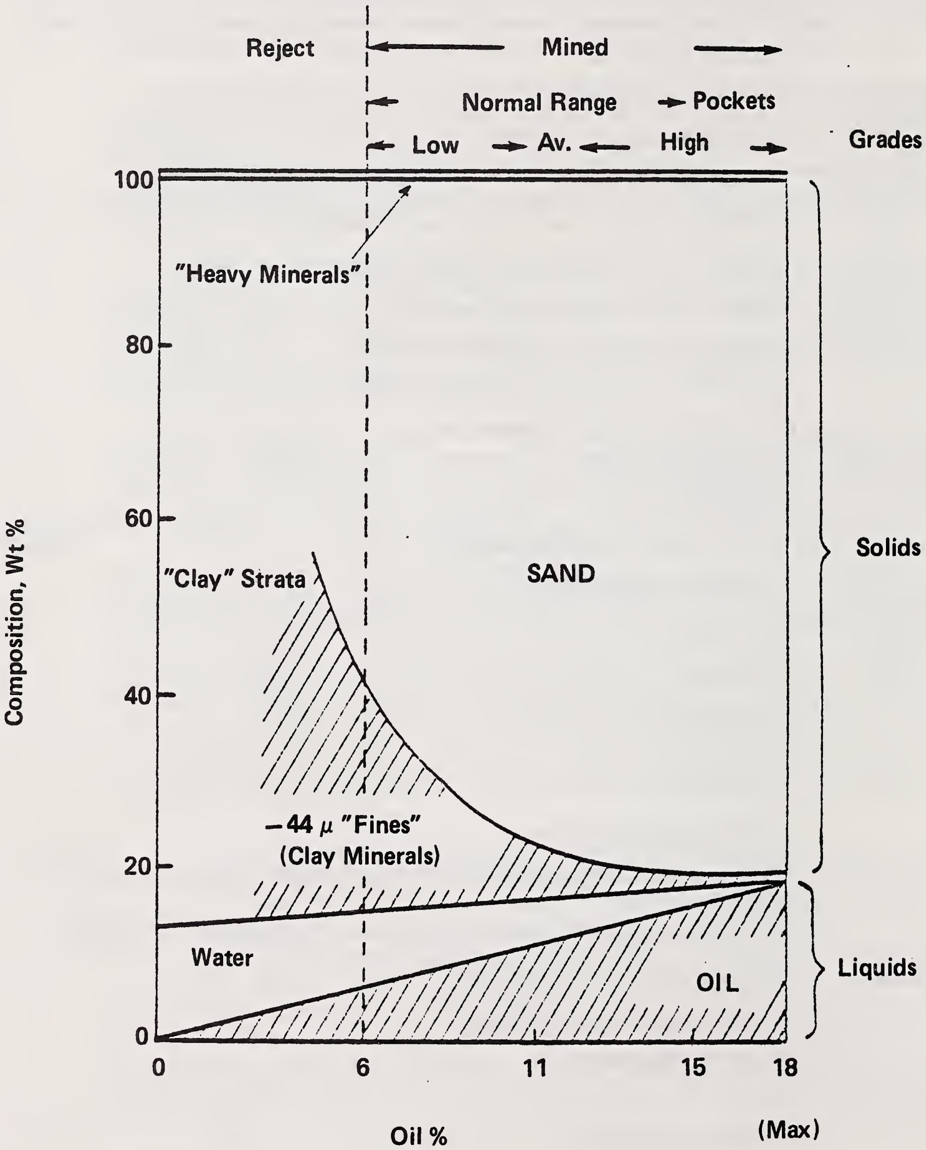


Table 1-2

General Inspections on Tar Sand Characterization samples

Core number	Area B	Hole 11	Hole 21A	-------- 15-16-2 --------			-------- 29-16-2 -------			------- 34-14-2 --------		
Depth	-	-	-	Top	Middle	Bottom	Top	Middle	Bottom	Top	Middle	Bottom
Footage	-[2]	-[3]	-[3]	67-99	115-163	163-214	32-63	63-110	110-174	79-110	110-159	174-206
Tar Sand Inspections												
Composition, Wt %												
Oil: Toluene Soluble	12.9	8.2	8.6	5.0	5.7	9.3	12.0	11.5	11.2	9.2	9.4	10.1
Acetone Soluble	0.12	0.09	0.13	0.10	0.10	0.09	0.10	0.11	0.08	0.07	0.10	0.10
Pyridine Soluble	0.11	0.13	0.20	0.22	0.20	0.09	0.05	0.13	0.08	0.19	0.15	0.21
Water	4.6	5.4	11.1	8.2	6.7	4.6	3.8	4.4	5.1	5.1	7.1	6.6
Fines (325-)	5.0	10.9	17.0	24.7	33.8	19.4	5.6	12.8	5.4	14.6	20.4	19.1
Solids (Total)	82.4	86.3	80.1	86.6	87.4	86.0	84.1	84.0	83.6	85.5	83.4	83.1
Iron on Extracted Solids	0.81	0.52	0.78	0.80	0.67	0.71	0.63	0.63	0.11	0.56	0.80	0.73
pH[1]	8.3	4.3	7.4	6.8	7.9	8.4	7.4	7.6	7.5	7.9	7.9	8.0
Heavy Minerals, Wt % on Solids[4]	0.5	1.0	0.6	0.5	0.5	0.4	0.8	0.4	0.2	0.5	0.6	0.3

(1) On 2-month old samples as pH meter was inoperable.
(2) Bottom of formation.
(3) Near top of formation.
(4) Separated in bromoform i.e. >2.9 g/ml

A general oil sand classification of behaviour and processability by area is used in discussion of Mildred Lake oil sands. An "Area B" type oil sand from the bottom of the formation in general implies a "high oil content" and separates well. An "Area D" type oil sand from near the top of the formation, e.g. Holes 9, 10, and 11, is "lower in oil - higher in fines", and does not process as well in separation. "Hole 21A" type oil sand has the "lowest oil and highest fines content" and exhibits poorest processability. However, significant differences in separation performance occur between samples from even the same general area. This again emphasizes that variability is not accounted for entirely by changes in the amount of one component, such as grade or fines present in the oil sands.

Beaver River oil sands, Table 1-4, also showed small differences of about 1% lower oil content for the same fines content compared to the correlation in Figure 1-2. Again, significant variations in composition are evident in this area even without without determining differences in the quality of the components.

Considering the application of an average composition of these data but realizing the gross inaccuracies that prevail using this limited amount of information on such a small random sample of oil sands, and assuming a 90 wt% overall oil recovery in separation, then mining of one square mile of this oil sand deposit for the production of 100,000 B/CD of bitumen would take about 5 years.

This exercise indicates that it is important to systematically obtain a great deal of information within a specific area that is selected for mining, to (a) assess the exact quantity of the oil available (b) define the types and behaviour of tar sands to be processed from time to time in a commercial operation, and (c) determine conditions that may be used when processing poorer quality tar sands to maximize oil recovery and froth quality, i.e. lowest contamination with water and solids. Further, the tar sand has a bulking factor of ~1.3.

Figure 1-2

Correlation of Oil Sand Composition

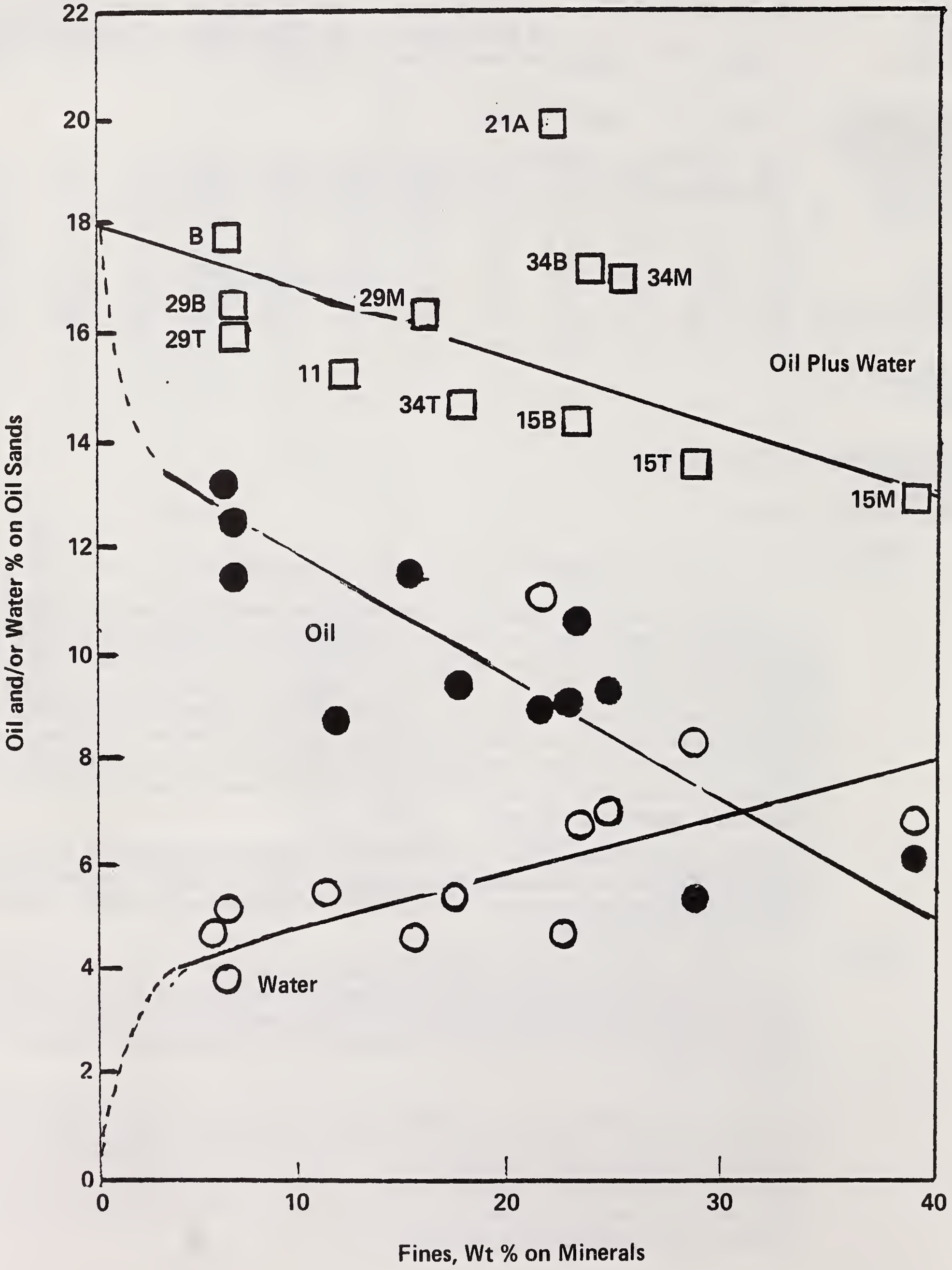


Table 1-3

Fines(Clay MInerals) can be mostly in Lenses or strata

Example: Homogenized oil sand with a spatula to <1/4" size, Soxhlet extracted 5% oil with toluene, dry screened total solids, gently grounds fractions in a mortar/pestle, and wet screened.

	g		g				
			Wet Screened Fractions				
Mesh Size	**Dry Solids**	**% Distribution**	**Sand (325+)**	**Fines (325-)**	**10+**	**Total**	**% Distribution**
10+	46.1	43	-	-	-	-	-
10-20	15.7	15	7.8	7.9	-	7.8	7
20-40	10.2	9	6.7	3.5	-	6.7	6
40-60	10.2	9	8.6	1.6	1.4	10.0	9
60-80	7.9	7	7.2	0.7	1.4	8.6	8
80-100	4.9	5	4.7	0.2	1.8	6.5	6
100-200	10.0	9	9.6	0.4	8.3	17.9	17
200-325	2.4	2	2.1	0.3	11.1	13.2	12
325-	1.1	1	-	1.1	22.1	37.8	35
Total	**108.5**	**100**	**46.7**	**15.7**	**46.1**	**108.5**	**100**

Table 1-4

Classification of Type and General Inspections on Beaver River Tar Sands used in Studies

Arbitrary Group	A	B				C		
Time Description	Old-Aged					New-Fresh		
Date Received, Sarnia	Nov 1964	1964			Nov 1964	Feb 1966		
Designation	Plant Feed	Good	Intermediate	Bad	Bench No. 1	Unit Feeds - Run No. 6	7	9
Sample Location Types Used In Blend of Composite	"Composite"	Representative of			Upper Few Feet of Deposit	Cut from Sept '65[1]	Bench No. 3 Nov '65[2]	30' South of Core Hole #1
Storage (Months) Prior to Shipping to Sarnia	Cold (?)				None	In Root Cellar (6) on Escarpment	(3)-Lab	None
Composition, Wt % on Tar Sand								
Water	4.0	2.0	2.3	3.7	3.4	4.9	3.0	4.5
Solids	85.0	87.1	88.2	89.9	85.6	85.5	87.4	86.0
Oil	11.0	10.9	9.5	6.4	11.0	9.6	9.6	9.5
Clay (325-)	16.3	21.2	17.1	18.8	12.0	11.0	15.1	14.3
Heavy Minerals (325+)	0.37	0.44	0.59	0.40	0.58	0.52	0.55	1.44

(1) Bench No. 3 tar sand stock piled (open to atmosphere) for several weeks before roughly homogenizing with mined Bench No. 5.
(2) Freshly exposed cut.

1-3 Summary

In summary, tar sand is a mixture of oil, sand, silt, clay, heavy minerals, carbonaceous fragments, water, gas, salts, and ions. The amount of these components in the tar sands vary appreciably, and the quality of the components has also been found to vary significantly, as will be discussed in the following sections.

In general, higher fines content and finer solids distribution result in lower oil content and higher water content. Other generalizations, based on these small samples of data used to illustrate the range of compositions that was encountered in these researches, are suspect.

2

OIL

Oil characterization in the petroleum industry usually emphasizes physical and chemical properties, such as gravity and viscosity that apply in crude handling; as well as sulphur, nitrogen, conradson carbon residue (CCR) and metal content, that affect refining. Surface properties are generally neglected because conventional crudes are normally produced with only a minor amount of emulsified brine that is removed in electrostatic desalting with chemical additives.

In the case of the oil from the oil sands, which is significantly heavier and contains more contaminants than other crudes Table 2-1, greater emphasis needs to be placed on the surface and chemical properties to understand its behaviour in separation from the oil sands, in contaminant removal, and in upgrading.

Studies aimed at a more fundamental understanding of the nature and behaviour of the oil are summarized in this section. The amount of data obtained was extensive and only examples are given to illustrate the general findings.

2.1 Physical Properties

2-1-1 Oil Gravity and Viscosity

Gravity measurements on oil extracted from tar sand samples taken from different areas at Mildred Lake are shown in Table 2-2. After extraction of oil with benzene, the oil-solvent mixture contains very small quantities of suspended mineral matter. Separation by centrifuging and solvent washing of this solid material has shown the separated solids to be a grey powder readily passing a 325 mesh sieve. The removal of this material by centrifuging prior to solvent removal was found to be important, as its presence in the extracted oil will affect gravity, CCR, and viscosity measurements. It is, also, necessary to correct quantities to a "solids free" basis. These values are shown in Table 2-2 and are based on an assumed density for "clay" of 2.2 g/ml. Further, the complete removal of benzene by 15/5 distillation is clearly important.

It is interesting to note from Table 2-2 that the $^{\circ}$API gravity of this selection of oils had an apparent trend that decreased with depth in the bed. This generality is suspect.

A gravity-viscosity relationship for oils extracted from the different Athabasca Tar Sands is shown in Figure 2-1. All these extracted oils were low in solids content, i.e. less than 1%. The measured gravity was corrected, as discussed in Table 2-2. The viscosity was corrected using Einstein's Equation, $\eta = \eta . (1 + kV)$ where $k = 2.5$ for spheres and V is the volume of particles in unit volume of mixture, assuming the solids to be non-solvated and spherical particles. Both these corrections are small.

These very limited data indicate the bitumen may be slightly lighter in the north than in the south. Again, this generality is suspect. Rather the form of the correlation is important that may have general application.

The oil gravity is very critical in flotation as can be seen from Figure 2-2. For instance, an oil of gravity greater than 8.5°API will just float on water at temperatures from 125 to 210°F. However, when the gravity is less than 8.5°API, the oil will sink. It is, therefore, surprising that the oil from Area B at the bottom of the formation, that has been found to have a gravity of about

Table 2-1

Quality Comparison with Conventional Crudes

Oil Source	Tar Sands	Coleville	Lloydminster	Weyburn - Midale	Redwater	Pembina
Gravity, $^{\circ}$API	9.7 - 6.5	14	15	29	35	38
Sulphur, Wt %	3.9 - 4.9	2.9	3.1	2.3	0.5	0.2
Viscosity SUS						
at 100°F	-	2270	-	53	46	41
at 210°F	329. - 2610	162	150	-	-	-
1000+$^{\circ}$F, LV %	50	47	35	19	16	13

Table 2-2

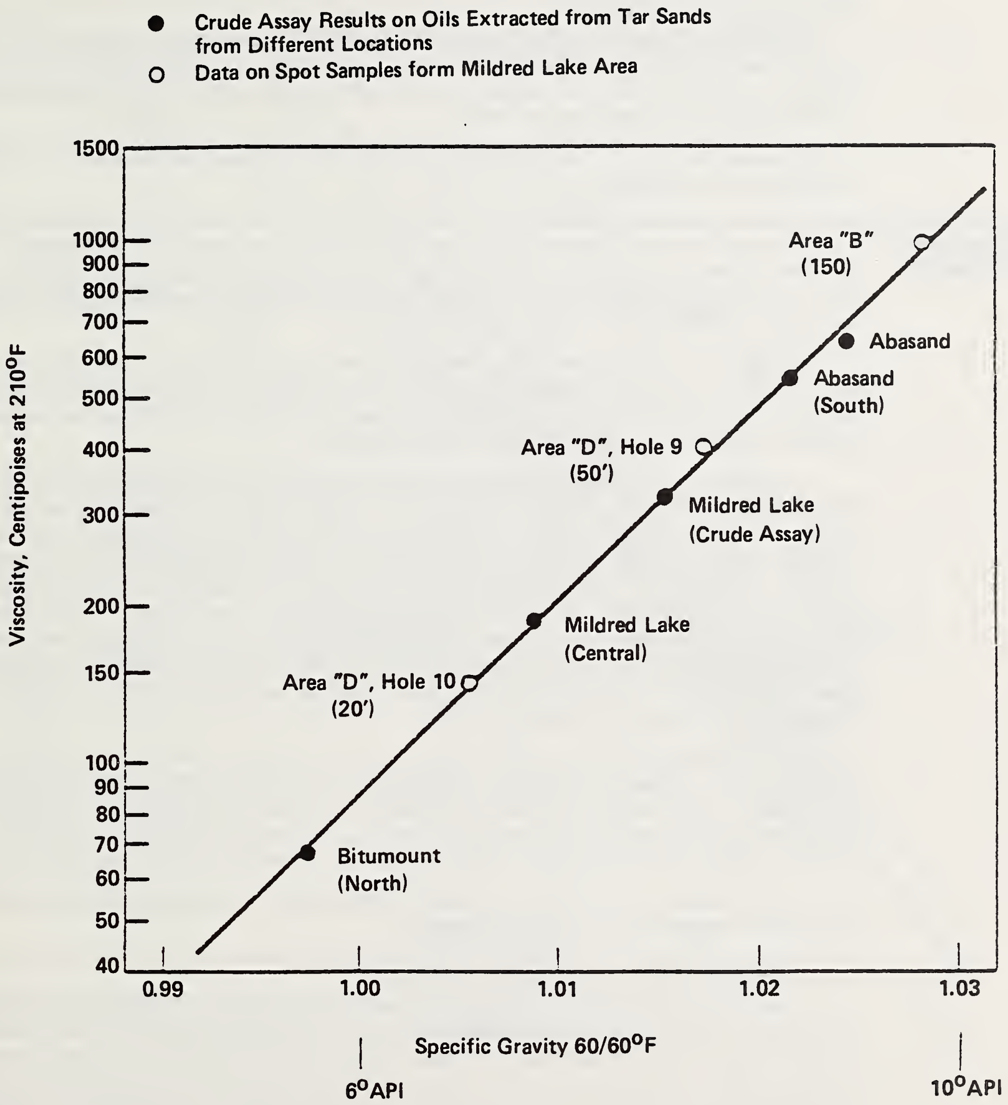
Gravities of Oils Extracted from Mildred Lake Tar Sands

Oil From Area	Hole No.	Gravity $^{\circ}$API	Dry Ash Wt %	Corrected (1) Gravity For Ash $^{\circ}$API	Approx. Distance In Feed From Top Of Escarpment (2)
D (3)	10	9.2	0.07	9.2	5
D	11	8.6	0.27	8.8	(35 Est.)
D (3)	9	7.2	2.07	8.6	50
D	9	7.6	0.05	7.6	50
B (3)	-	6.1	0.08	6.1	150
B	-	2.2	4.85	5.3	150

(1) Using 2.7 g/cc for ash (i.e. clay)
(2) Not including any overburden at top of exposed face.
(3) Samples taken at same time. Other samples and exact location were not specified in shipping instructions.

Figure 2-1

Gravity-Viscosity at 210 °F Relationship for Oil from the Athabasca Tar Sands (both measurements corrected for ash contents)



6.0°API, separates so well in the hot water separation process. Presumably, connate gas and aeration play an important role here to effect excellent oil recoveries with this type of oil sand (Section 6). However, the general comparison, Figure 2-2, indicates that bitumen gravity can be a factor in separation by hot water flotation.

2-1-2 General Inspections

The typical qualities of benzene extracted bitumen from tar sand samples taken from the exposed formation along the Athabasca River are compared, together with distillate fractions, in Table 2-3. It will be noted that sulphur (4.6 wt%) and nitrogen (0.4 wt%) are high, and only 50 wt% of the total oil distills below 1000°F.

In general the oils from north and south appear similar but heavier and more viscous. Again this generality is suspect.

2-2 Chemical Composition

Elemental analyses of three oils extracted from different tar sands from the Mildred Lake area are shown in Table 2-4. It can be seen that the hydrogen content is not high, e.g. H/C = 1.49 - 1.55, compared to H/C = 2.0 for typical petroleum products. Illustrating the need to remove carbon and/or add hydrogen in upgrading.

Sulphur as well as nitrogen contents are high relative to other crudes that indicate the need for more difficult and severe upgrading to useful products. Although the recoveries are indicated to be ~100%, the crude contains a small but significant amount of oxygen that was not measured directly in these preliminary inspections on these samples.

An example of an infrared adsorption spectrum of a toluene extracted oil from the Hole 11 tar sand, centrifuged and filtered to contain only colloidal solids associated with the oil, i.e. <0.5μ, is shown in Figure 2-3. Infrared spectra on all the other eleven characterization study samples, Table 2-6, were similar to the example shown. The adsorption at ~3.4-3.5 (strong), ~6.8-7.0 (strong), ~7.2-7.3 (medium), and ~8.5-8.9 (weak) are indicative of C-H type structures. The adsorption at ~6.1-6.4 is typical of ring type structures. The adsorption at ~5.8-6.0, together with the broadening between 3-4 microns, is typical of a carboxylic acid with hydrogen bonding and possible carboxylate salt formalizing. Amines would not be expected as they are not normally found in crude oil. More likely the nitrogen is present as heterocyclic, such as porphyrin type structures with central metal ions e.g. Ni, VO^+.

Strong adsorptions at ~8.0, ~9.2, ~9.8 and ~12.3-12.5 microns were observed in many infrared spectra of oil samples containing small quantities of solids, and also asphaltene fractions precipitated with n-pentane from these oils. Removal of solids by centrifuging and filtering to <0.5μ resulted in a sharp decrease in these adsorptions. The removed solids were identified as α quartz and clay minerals are also reported in the literature to exhibit these infrared adsorptions.

It was concluded that scrupulous removal of contaminants is necessary to obtain sound fundamental measurements on oil sand components.

2-2-1 Component Compositions

Composition analyses using attapulgus clay and silica gel adsorption methods for separating the saturate, aromatic, resins and asphaltene (SARA) components of the oil are also shown in Table 2-5. The results are significantly different indicating that the definition of components is very dependent upon the method used to separate these components. As will be shown in the next section, more distinct component definition is obtained using the attapulgus clay method. The elemental component distributions amongst the components separated by the clay method are shown in Table 2-4. Sulphur and nitrogen are distributed mostly among the asphaltenes and resins.

In general, molecular weight measurements appear inconsistent, that is thought to be due to association of multiples of basic unit structures. For example, molecular weights of resins are typically ~1500, but Area B resin is slightly more than half this value. If it is assumed that the Area B resin is a basic component structure, typically resins implies association of 2 units.

Figure 2-2

Relative Density Relationship for Water and Oil from Mildred Lake Tar

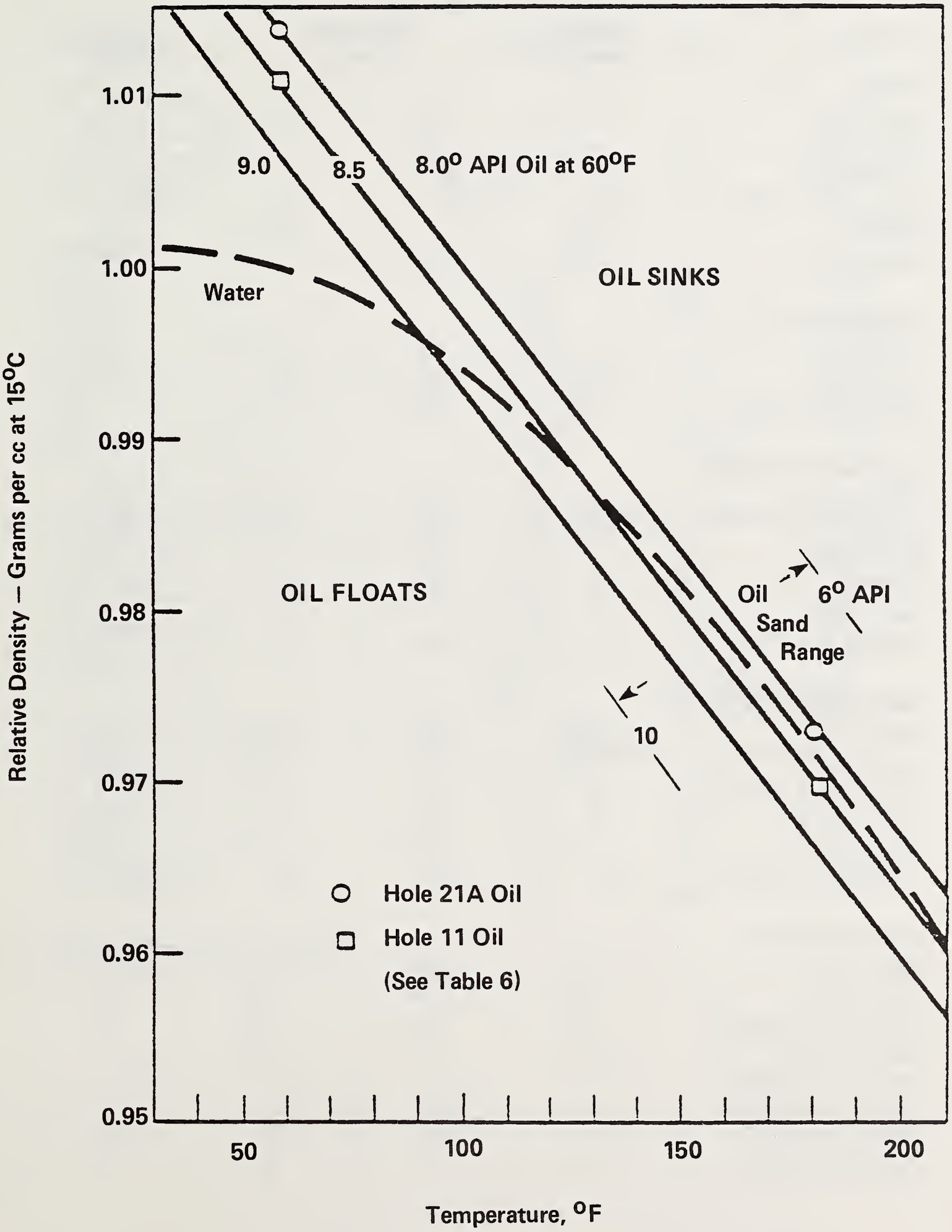


Table 2-3

Inspections on Oils

Oil From:	Bitumont (North)	Mildred Lake (Central)		Abasand (South)
Total Oil				
Gravity, °API	9.7	7.8	8.6	6.5
Sulphur, Wt %	4.2	4.8	4.4	4.9
Pour Point, °F	35	85	45	100
Viscosity SU at 210°F	329	1623	913	2610
CCR Wt %	11.6	-	13.6	15.5
Nitrogen Wt %	0.39	0.48	0.29	0.40
Naphtha C5-430°F				
Yield, LV %	2.9	1.7	1.7	1.0
Gravity, °API	38.8	34.8	34.7	35.7
Sulphur, Wt % Lamp.	0.6	0.35	0.5	-
Light Gas Oil 430°-650°F				
Yield, LV %	17.9	11.3	13.5	10.5
Gravity, °API	25.5	25.9	25.9	25.4
Sulphur, Wt %	2.1	1.6	1.6	1.6
Pour Point, °F	-50	-55	-70	-55
Diesel Index	-	-	-	-
Viscosity, SU at 100°F	45	49	47	46
Heavy Gas Oil 650°-980°F				
Yield, LV %	29.9	32.2	32.2	35.9
Gravity, °API	13.8	14.8	14.2	13.0
Sulphur, Wt % Dietert	2.4	3.4	3.2	3.7
Pour Point, °F	20	25	10	30
Nitrogen, Wt %	0.11	0.20	0.10	0.24
Viscosity, SU at 100°F	1708	1975	1137	2728
Residuum 980°F+				
Yield, LV %	49.3	54.8	52.5	52.6
Gravity, °API	0.1	0.9	1.0	-1.0
Sulphur, Wt % Dietert	6.6	6.2	5.6	5.9
Nitrogen Wt %	-	0.7	0.6	-
Viscosity, SF at 250°F	210	-	-	554
Viscosity, SF at 275°F	-	1850	too heavy	-
Softening Point, °F	172	168	168	195
Penetration, at 77°F	7	4	6	2

Table 2-4

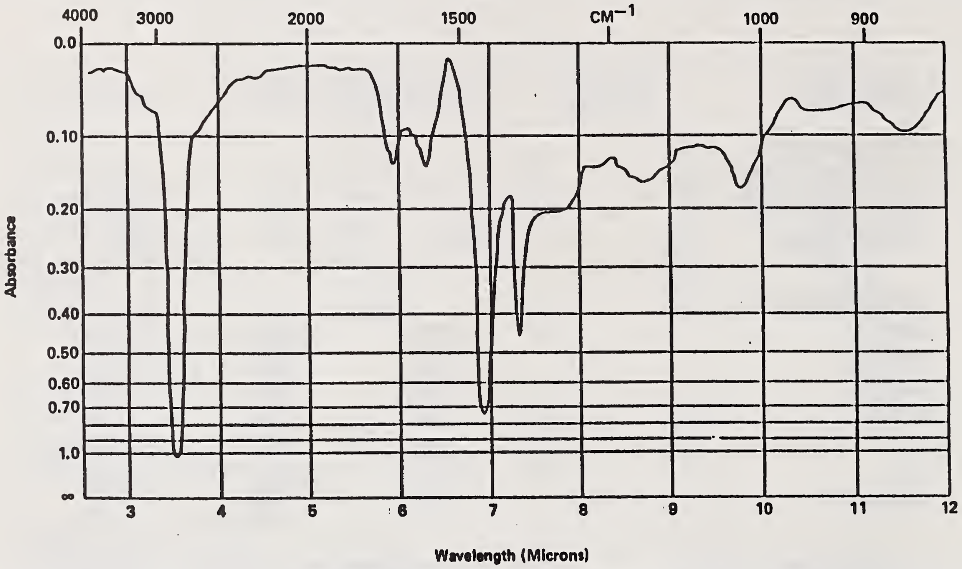
Inspections Extracted Oil(1) from Characterization Tar Sands

Tar Sand From:	Area B	Hole 11	Hole 21A
Oil(1) Inspections			
Gravity, °API at 60°F	7.2	8.5	8.0
Gravity, °API at 180°F	-	14.4	14.0
Molecular Weight	769	678	672
Components, Wt %			
Carbon	83.10	83.15	83.10
Hydrogen	10.52	10.85	10.40
Nitrogen	0.58	0.46	0.49
Sulphur	5.10	4.84	4.75
Ash	0.73	0.88	1.44
Total	100.03	100.18	100.18
H/C Ratio	1.51	1.55	1.49
Oil Composition, Wt %	**-- Attapulgus Clay Adsorption Method --**		
Saturates, Wt %	14.9	15.4	15.2
Aromatics, Wt %	11.9	14.2	19.1
Resins, Wt %	49.9	43.3	42.4
Asphaltenes, Wt %	17.3	17.9	22.9
Recovery, Wt %	94.0	90.8	99.6
M Wt of Asphaltene	2560	2725	2210
Oil(2) Composition, Wt %	**-- Silica Gel Adsorption Method --**		
Saturates, Wt %	30.1	26.7	33.0
Aromatics, Wt %	33.9	38.5	38.3
Resins, Wt %	7.2	12.1	8.5
Asphaltenes, Wt %	23.6	17.6	15.2
Recovery, Wt %	94.8	94.9	95.0

(1) Extracted with benzene and then acetone.
(2) Oil extracted with toluene.

Figure 2-3

Infrared Adsorption Spectra of Toluene Extracted Oil from Hole11 Tar Sand Containing < 0.5 Material



The structure of the asphaltene are most probably porphorin. Presumably these basic structures are associated with other chemical units that are reflected in higher molecular weights.

Analyses on a wider range of Athabasca oils are shown in Table 2-6.

2-2-2 Polar Components

In addition to saturates, aromatics resins and asphaltene components of the bitumen, there is a 5th component class that is comprised of interfacially active polar compounds. These components tend to come out of solution in bitumen, diffuse to oil-water interfaces, and depending on the pH condition dissolve to some extent in the aqueous phase, ionize, adsorb on active sites of the oil sand solids, effect solid-oil contacting, spread at gas - water interfaces to occlude gas into the oil, reduce the interfacial tension of the oil, attract ions from the aqueous media to the interface, and form salts, etc. This multi-behaviour will be discussed in more detail.

These components that range in molecular weight are considered to be one class of compounds as infrared spectra or polar compounds (1) adsorbed on solids, (2) recovered from water phases, (3) films from water/bitumen interfaces, are similar and appear to be a general class with a common functionality of carboxylic-carboxylate groups. The amount present in an oil sand varies, and is quite small in the order of a few percent.

2-2-3 Adsorption on Solids

It was shown in Table 1-2 that about 1-2 wt% of the total oil in tar sands is not extracted with aromatic solvents such as benzene and toluene, but acetone washing removed part of these polar hydrocarbons, but pyridine was more effective. Although, the differences are small between samples, it may be noted that there is a very slight trend toward poorer processability with higher benzene insolubles. These polar hydrocarbons are strongly adsorbed on the solids either in the material state of the oil sand, or when the water films are removed in the soxhlet extraction used to separate and recover the oil sand components. Their association is proposed to take place on active sites of adsorbed polyvalent ions e.g. Fe^{++}, Ca^{++}, and is one of insoluble car-

Table 2-5

Composition of Oil Components from Characterization Tar Sands Attapulgus Clay Separations

Tar Sand from Fractions from Composition, Wt %	Area B	Hole 11	Hole 21A
Saturates			
Carbon	86.95	85.50	86.10
Hydrogen	13.80	13.43	13.61
Nitrogen	-	-	-
Sulphur	0.28	0.15	0.11
Ash	0	0	0
Mol Wt(1)	600	-	-
Aromatics			
Carbon	85.50	85.55	84.50
Hydrogen	11.47	10.95	10.63
Nitrogen	-	-	-
Sulphur	2.79	3.87	3.77
Ash	1.62	0	<0.25
Mol Wt(1)	470	-	-
Resins			
Carbon	79.30	81.45	79.80
Hydrogen	9.64	9.98	9.97
Nitrogen	0.63	0.54	0.54
Sulphur	7.20	5.12	6.07
Ash	<0.25	<0.25	<0.25
Mol Wt(1)	845	-	-
Asphaltenes			
Carbon	79.30	79.40	77.60
Hydrogen	8.18	8.44	8.13
Nitrogen	1.17	1.15	1.11
Sulphur	8.30	7.90	8.52
Ash	1.15	1.44	2.36
Mol Wt(1)	2560	-	-

(1) By Mechrolab Osmometer on small samples.

Table 2-6

Inspections on Oil and on Alphaltene Component from Characterization Tar Sands

Core Number	Area B	Hole 11	Hole 21A	-------- 15-16-2 --------			-------- 29-16-2 -------			-------- 33-14-2 -------		
Depth	-	-	-	Top	Middle	Bottom	Top	Middle	Bottom	Top	Middle	Bottom
Footage	-	-	-	67-99	115-163	163-214	32-63	63-110	110-174	79-110	110-159	174-206
Oil Inspections												
Oil Composition, Wt %	**SARA Analysis (No Recycle)**											
Saturates	12.1	11.6	12.1	9.5	11.2	13.7	11.6	14.7	13.8	9.7	14.3	10.6
Aromatics	21.6	13.7	20.3	0.7	1.3	6.2	8.5	3.9	2.7	0.6	4.6	5.3
Resins	50.4	55.9	59.4	59.5	60.1	57.4	62.6	55.0	54.8	56.6	52.7	63.6
Asphaltenes	18.4	16.8	16.1	19.0	17.3	19.5	17.3	18.1	21.3	22.6	18.1	20.5
Recovery	102.5	98.0	107.9	88.7	89.9	96.8	-	91.7	92.6	89.5	89.7	-
Metals, ppm	**X-ray Fluorescence Analysis**											
Iron	67	30	93	43	63	58	62	68	80	72	54	50
Nickel	72	54	60	52	60	68	60	62	69	62	60	67
Vanadium	365	279	319	247	288	371	325	345	411	328	328	368
M Wt by Mechrolab Osmometer	-	-	-	661	-	-	-	-	779	-	685	-
Asphaltene Inspections												
Components, Wt %												
Carbon	77.40	71.20	76.90	79.50	78.30	78.70	78.10	78.30	77.15	77.95	78.60	79.50
Hydrogen	7.70	7.49	7.91	8.23	8.08	8.15	7.97	7.86	8.10	8.05	8.22	8.06
Nitrogen (Coleman)	1.01	1.16	2.36	1.27	1.87	1.57	2.10	1.67	1.49	1.40	1.58	1.04
Sulphur (Leco)	7.95	7.15	7.73	7.86	8.08	7.95	7.85	7.54	7.62	7.75	7.85	7.68
Ash	3.22	9.59	3.65	1.52	1.45	2.50	2.42	3.20	1.30	1.12	1.29	1.06
Total	97.28	96.59	98.55	98.38	97.78	98.87	98.44	98.57	95.66	96.27	97.54	97.34
Atoms/100 Atoms of Hydrogen	**Calculated**											
Carbon	84.3	80.0	81.7	81.1	81.4	81.1	82.1	83.5	80.0	81.2	80.3	82.7
Nitrogen	0.9	2.5	2.1	1.1	1.7	1.4	1.9	1.5	1.3	1.2	1.4	0.9
Sulphur	3.2	3.0	3.1	3.0	3.1	3.1	3.1	3.0	3.0	3.0	3.0	3.0
Oxygen (By Difference)	2.2	2.9	2.9	1.2	1.7	0.9	1.2	1.2	3.4	2.9	1.9	2.1
Components of Ash, Wt %	**Semi-Quantitative Emission Spectrograph**											
Major 10% or greater	Si	Al,Si	Si	-	Si	Si	Si	Si	Si	Si	-	-
Large minor 5-10%	-	-	Al	-	-	-	-	-	-	-	-	-
Small Minor 1-5%	Al	-	-	Si	-	-	-	-	Al	-	Si	Si
Large trace 0.2-1%	Ni,Fe V,Ti	Fe,V Ti	Ni,Fe V,Ti	V	Fe,Al V,Ni,Ti	Fe,Al,V Ni,Ti	V,Fe Al,Ti	V,Al Fe,Ti	Ni,Fe V,Ti	Fe,Al V,Ti	V	V,Al
Small trace less than 0.2%	Ba,B Mg,Mo Cu,Ca	Ba,B Mg,Mo Cu,Ca Ni	Ba,B Mg,Mo Cu,Ca Cu,Ni	Ti,Ba B,Mg Fe,Al Cu,Ni Mo,Cu	Ba,B Mg,Mo Cu,Ca	Ba,B Mg,Mo Cu,Ca	Ba,B Mg,Mo Cu,Ca Ni	Ba,B Mg,Mo Cu,Ca Ni	Ba,B Mg,Mn Cu,Ca	Ba,B Mg,Mo Cu,Ca Ni	Ba,B Mg,Fe Ti,Al Mo,Ca Ni,Cu	Ba,B Mg,Fe Ti,Mo Cu,Ni Ca
M Wt by Mechrolab Osmometer	-	-	-	1590	-	-	-	-	2660	-	1945	-

boxylate salt formation. As both acetone and pyridine complex with basic cations, the surfactants are removed by these solvents through a mechanism of exchange.

It may be noted at this point that if the tar sand solids, after extraction with benzene, are contacted at 140°F with dilute NaOH solution, pH = 9.0, and filtered, an intense blue fluorescence is developed in the clear NaOH solution when irradiated with UV light. This indicates that NaOH removes at least part of the pyridine soluble polar hydrocarbons into solution, presumably again by exchange and the formation of soluble sodium carboxylates. The application of UV fluorescence to measure oil in aqueous solutions is discussed in the next part of this section.

2-3 Aqueous Soluble Oil

Partial solubility effects in polar solvents and aqueous solutions were evaluated using mainly ultra-violet fluorescence as a measure of solubility. At the low solubilities encountered, one unit of fluorescence corresponded approximately to 1 wppm of oil in the aqueous phase as measured by solvent extraction and recovery of the dissolved oil from neutralized solutions.

2-3-1 Polar Solvents

High hydrogen bonding solvents, such as ethanol and isopropanol, gave blue fluorescent solutions in contact with the total oil. Methanol solutions from oil extraction were green-blue, indicating solubility of an additional oil component, that was confirmed by paper chromatography.

Infrared adsorption spectra on the blue florescent alcohol extracts as well as on pyridine extracts from oil associated with (benzene soluble oil free) solids were found to be similar to oil that is soluble in basic solutions. As will be discussed later, this specific class of polar components again contained principally a carboxylic functional group in an aliphatic type molecule.

2-3-2 Aqueous Solutions

The ultra-violet fluorescent of acidic and basic aqueous solutions, after contacting with oil, for 3 days at 75 and 150°F, was measured and used to assess the relative oil solubility in these aqueous phases. This latter temperature was used to simulate the temperature, of hot water separation of the oil sands. For most solutions, "equilibrium" fluorescence was attained in less than 24 hours. Three days were used experimentally to ensure "equilibrium" at the lower ambient temperatures with the viscous oil. The oil sand formation temperature was not simulated, because of uncertainty in time to reach equilibrium under these conditions.

The initial and final pH of the contacting solutions with two different oils from different locations in the Athabasca formation are plotted against the ultraviolet fluorescence generated, Figures 2-4 and 2-5. Only under very basic and acidic conditions was high fluorescence or high oil solubility achieved. Comparing the y-axis scales of the upper and lower plots show an expected higher oil solubility at the higher temperature. Extrapolation of the temperature effect would indicate even higher oil solubility in water at higher temperatures e.g. in situ steam drive.

The fluorescence increased slightly with increasing pH from 3 to 10 for both oils. Hole 11 oil gave more soluble polar hydrocarbons in the aqueous solutions. This is consistent with a higher quantity of higher polar resin compounds in the oil, i.e. 8 wt% for Hole 11 oil versus 13 wt% for Area B oil, Table 1-2. Hence, a typical amount of surfactants in the aqueous phase during hot water flotation is shown in the bottom plot in Figure 2-4 at 8 pH for both good and poorer (oxidized) processability type tar sands.

Comparing the 2 sets of data in Figures 2-4 and 2-5, shows the solution pH was compressed after oil contact. This is also shown more clearly in Figure 2-6, where the pH can be seen to tend toward an equilibrium value. Similar shaped figures were obtained for both oils, but the equilibrium pH was 7 at 75°F, and 8 at 150°F. 8-9 pH is quite characteristic of the usual pH of hot water flotation separation. The curves at both temperatures show the oil is behaving as an amphoteric, that is both acidic and basic solutions tend to be neutralized by the oil going into solution. The reaction of caustic in solubilizing these polar oil components is clearly shown in Figure 2-6.

Figure 2-4

Relative Fluorescence of Acid and Base Solutions in contact with Oil at Different Temperatures

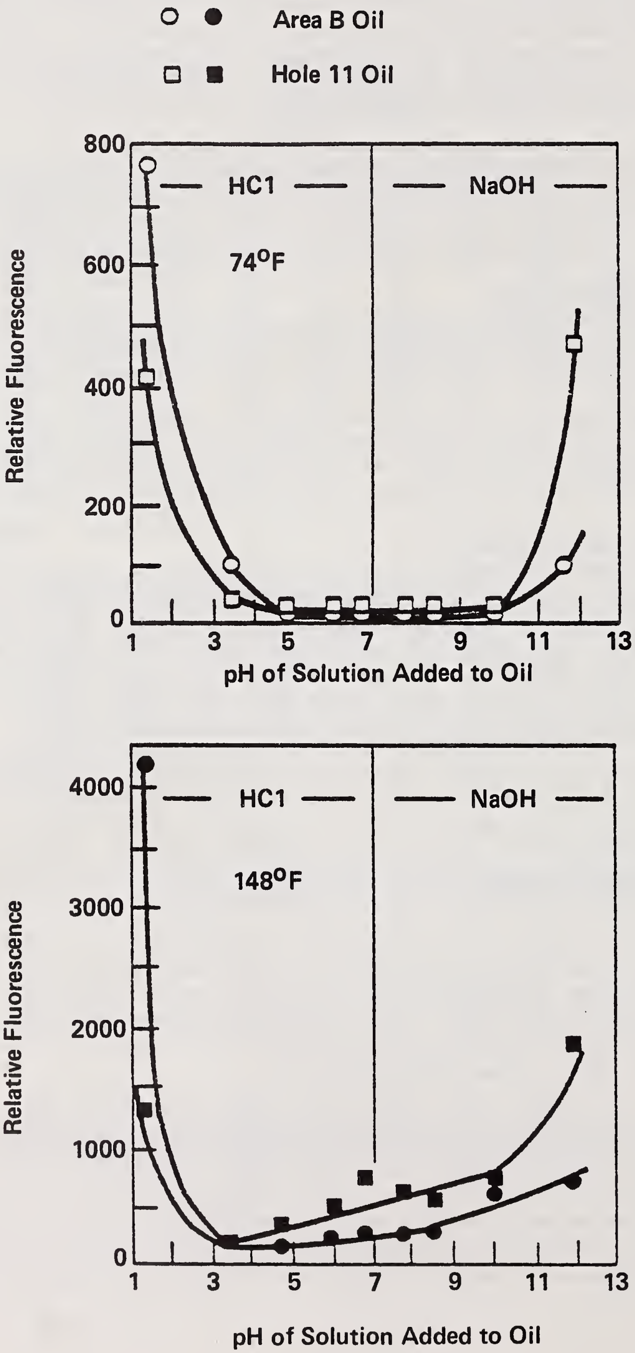


Figure 2-5

Relative Fluorescence of Acid and Base Solutions in contact with Oil at Different Temperatures

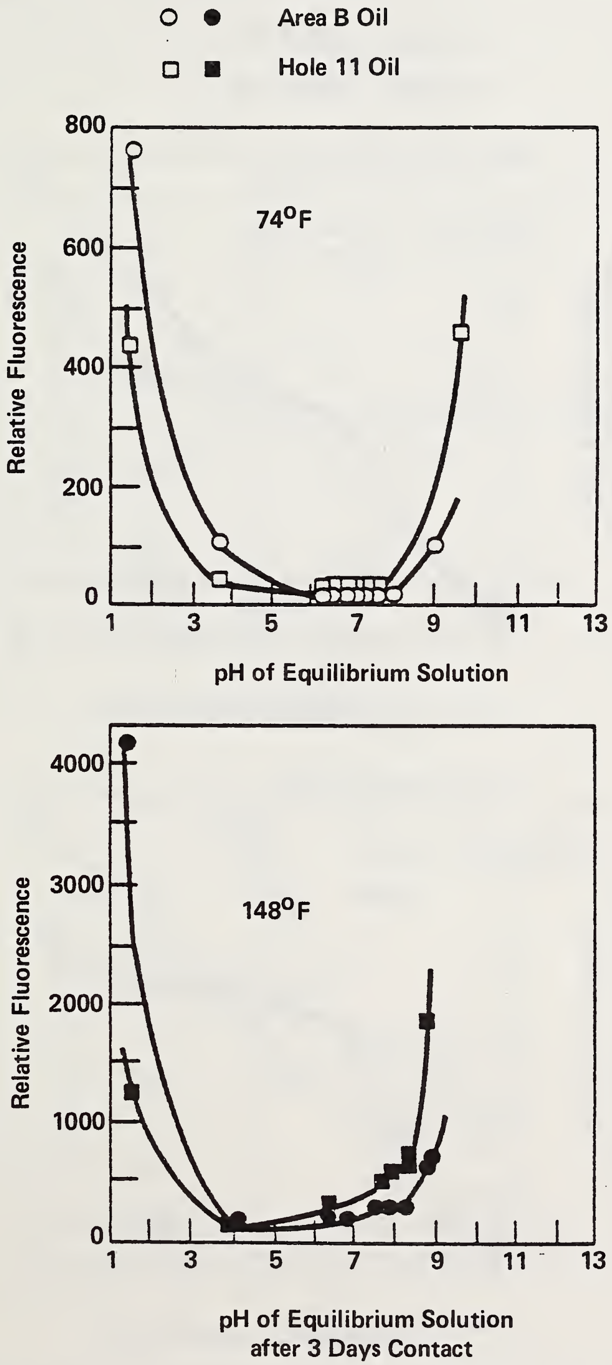


Figure 2-6

Effect on pH of Acid and Base Solutions in contact with Oil at Different Temperatures

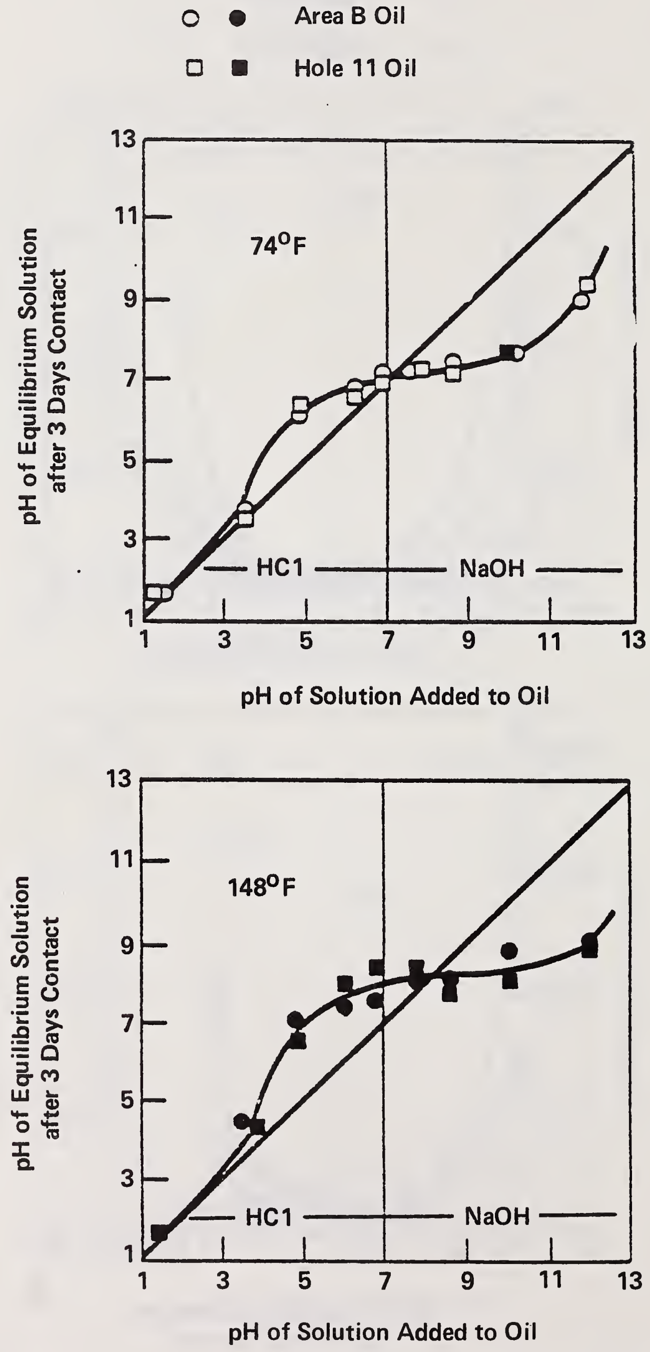
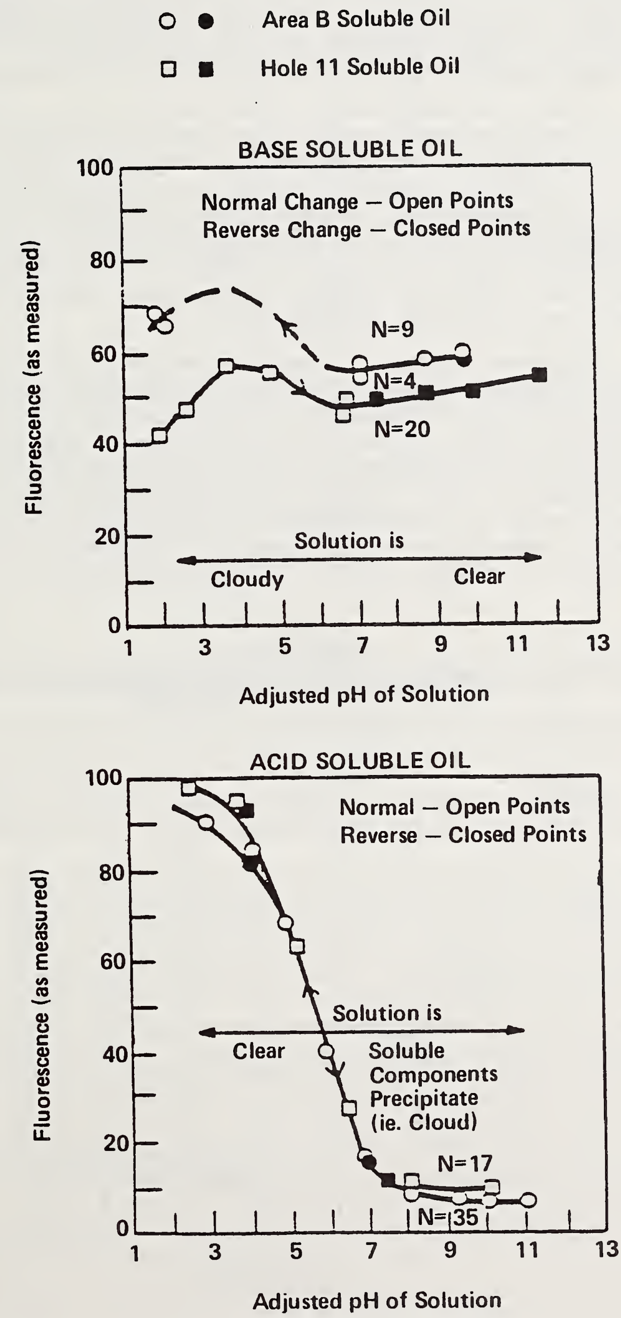


Figure 2-7

Fluorescence Behaviour of Acid and Base Soluble Components of Oil

(N = Number of Sample Dilutions)



2-3-3 Amphoteric Nature

The amphoteric behaviour of the oil is not necessarily centered in one component molecule, but rather in a mixture of different polar components of the oil. This is illustrated by the data in Figure 2-7. The upper plot shows the change in fluorescence of a base soluble oil component on adjustment of the pH to acid conditions and then reversing the pH back to basic conditions. It can be seen that the fluorescence does not change significantly with pH in spite of a tendency to come out of solution in acid media. The fluorescence appears to be a function of the molecular structure of the component with little contribution from the solubilizing group.

The lower plot shows the change in fluorescence that occurs on changing the pH of the solution of an acid soluble oil component. Here a dramatic fluorescence reduction occurred on increasing the pH. The solution became slightly cloudy in basic media, indicating that the oil component is coming out of solution. Reversing the pH resulted in the original high fluorescence, and disappearance of the oil cloud. The significance of the behaviour of the acid soluble oil is in pH adjustment of acid oil sands to slightly alkaline conditions of hot water flotation process. The acid soluble material, that can cause flocculation of oil and solids and hence reduces oil yield in acid media, is salted from alkaline solution rendering it inactive. The data also indicates sensitivity of the hot water separation process to pH.

Comparison of the two sets of data show these base and acid soluble oil components are significantly different. Isolation of both the acid and base soluble oil components was effected by ether extraction of equilibrium solutions after neutralization. The infrared pattern of the base soluble oil is shown in Figure 2-8. Strong carboxylic acid peak at about 5.8 microns together with characteristic broadening of the upper part of the peak at about 3-4 microns. There is also an indication of an ester groupings from the slight co shift to lower wavelength. Nuclear magnetic resonance confirmed the presence of labile hydrogen, and indicated a saturate-naphthene structure rather than an aromatic condensed ring hydrocarbon. An average molecular weight by osmometry was ~250 indicating ~15 carbon atom compound. Other surfactants fractions

Figure 2-8

Infrared Spectra of an Extracted Base Soluble Oil (Extracted from Area B with a 11.5 pH - NaOH Solution)

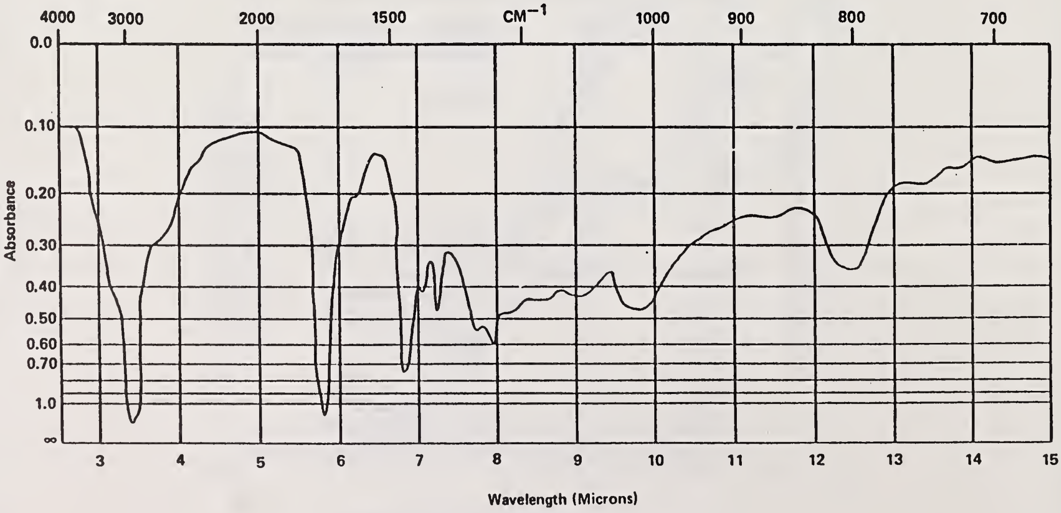
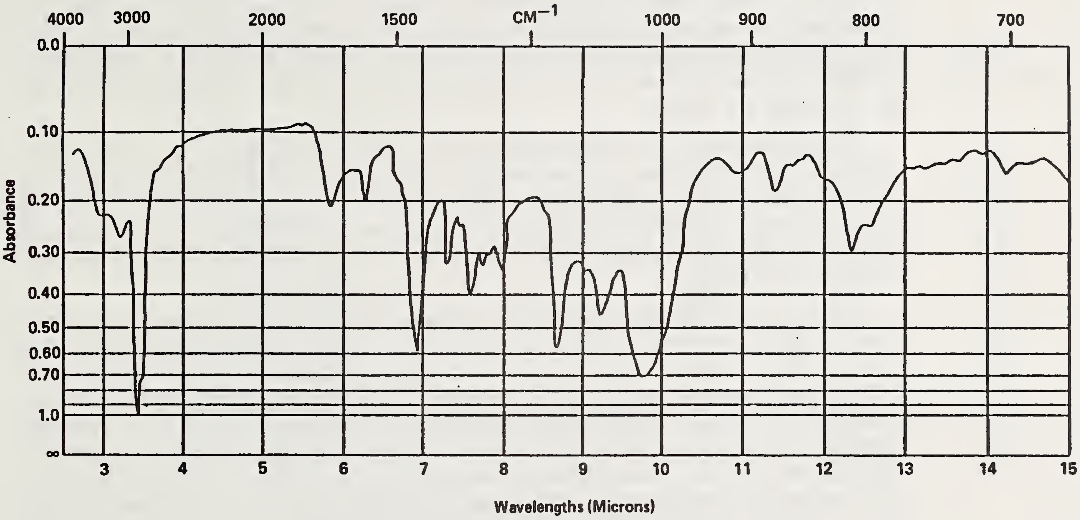


Figure 2-9

Infrared Spectra of an Extracted Acid Soluble Oil (Extracted from Hole 11 with a 1.5 pH - HCL Solution)



recovered by solvent extraction from solids have indicated higher molecular weight of ~400. Hence a broader range of molecules type work probably occur.

A carboxylic acid structure is also consistent with the fluorescent data, since a carboxyl grouping would not contribute much to resonance with ring systems in the molecule. It is interesting that similar spectra to the base soluble oils were found for pyridine extracts of oil sand solids that were free of benzene soluble oil, as well as alcohol soluble oil, thus substantiating the interfacially active nature of these carboxylic-carboxylate components, as pointed out before.

The infrared spectra of the acid soluble oil component is shown in Figure 2-9. This material was distinctly different, complex, and closer to a resin type in structure, see Appendix V6 A 18. Although some carboxylic-carboxylate groups are indicated, there is strong evidence of nitrogen groupings, such as NH, indicated by the peak at 2.8-3.2 microns. This is substantiated by a nitrogen content determination of 1.2 wt%. A more aromatic condensing system is indicated, than the base soluble oil, that was also supported by nuclear magnetic resonance measurements. Further there is evidence in the 9-10 micron range of sulphur-oxygen bonding either in the same molecular structure or in separate molecular components. This C-S bonding was thought to be the site of oxidation during the aging process because of the much more rapid rate than would be expected for C-C bonds.

2-3-4 Interfacial Dynamics

As most oil sands are slightly alkaline and in a reduced state, that is they have not undergone oxidation by air exposure generating detectable acid conditions, then the base soluble carboxylic-carboxylate oil is interfacially operative in most oil sands and in physical separation of the phases. These interfacial components film readily facilitating the occlusion of air in bitumen during slurry with hot water that is needed for flotation in the carefully balanced energy process of flotation. On the other hand, direct air addition is detrimental in producing high solids froth, as the soluble surfactants in equilibrium with those in the interface act as typical flotation collectors for the solids.

A number of interesting observations have been made with oil droplets in cold distilled water. The oil was extracted from the tar sands with benzene, centrifuged essentially free of solids, and the solvent removed by distillation. If care was taken to exclude the air, i.e. forming the oil droplet under water using a hypodermic syringe, the blob was very oily and tacky. In a short time, it became water wet, due to the formation of a protective skin at the oil-water interface, from diffusion of components from the interior of the oil to the interface. Indentations in the blob could now be made by both hydrophilic (glass) and hydrophobic (carbon) rods without the oil sticking to the rods.

If the oil droplet was formed occluding small quantities of air, the protective skin was torn off after long standing at room temperature, by the action of the air being released from the oil. A thin plastic-like film now formed on the surface of the water, which wrinkled and buckled when a force was applied laterally, i.e. condensed film. This was invariably observed in many pendant drop measurements of interfacial tension. Also, when disrupted and broken, the film would slowly (1-2 seconds) reform.

In some experiments, the oil sample was contaminated with rust that contains some ferrous iron. The skins formed at the surface disengaged readily. These plastic-like films dried, on exposure, to a solid parchment-like layer containing small particulate material that shattered readily. These skins would be analogous to the formation of insoluble heavy metal soap laminar films. The different behaviour resulted from combination of the iron component with the surfactant, that was less soluble in the oil, and gave the film different, more rigid, properties. Air bubbles in the water showed some tendency to adhere more readily to the surface of these films, which suggests that the iron was acting as a bridging agent increasing induction time and facilitating the occlusion of air. It is speculated, that, this may be a factor in preconditioning oil sands in slurrying prior to flotation.

These films appear to be the same as those that form sacks filled with water in oil froth and require dilution and centrifuging to overcome the self-adhesion and release the occluded water. Infrared spectra were essentially the same as the base soluble oil, Section 2-3-3. Hence, these naturally occurring, more aliphatic surfactants are anionic at the slightly alkaline conditions of 8-9 pH of the oil sands that is consistent with the high negative charge measured on bitumen particles that will be discussed later.

2-3-5 Soluble Oil

The existence of soluble oil in the water phase from hot water extractions was observed by UV fluorescence of the clear phase, after acidifying to flocculate the clay, and then removing the clay by centrifuging. The aqueous solution exhibited varying amounts of fluorescence as summarized in Table 2-7 for the tar sands used in the characterization study, Table 1-2.

The fluorescence for most of the samples obtained from alkaline tar sands are low. It is suspected that the soluble oil which comes out of solution on acidification, indicated before as a cloud, was carried down with the centrifuged flocculated clay. The removal of clay being necessary to the measurement of fluorescence. The acidic Hole 11 tar sand, i.e. no acidification used, exhibited the highest fluorescence, which tends to substantiate this point. *(Appendix V6)*

In the preparation of a clarified water phase, three filters were used. The purpose of the first, 0.8μ, was to eliminate most of the particulate material and improve subsequent filtering rates. The resulting water phase was then filtered through 0.45μ, i.e. closest filter size available to comply with the definition of colloid as material of less than 0.5μ. Final filtration through 0.2μ was carried out to eliminate any traces of suspended clay minerals and to obtain a clear solution for colloidal oil and salt determinations after centrifuging.

The bulk of the material removed on 0.2μ filters from alkaline water phases was oil. After solvent extraction, only fine membranes containing some solids were left, indicating that the amount of colloidal clay was very small. Although fresh core hole samples from the Beaver River area were found to give more colloidal clay.

Table 2-7

Relative Fluorescence of Separated Water Phase after Removal of Fines(1)

	pH		
Water Phase From Separation With Tar Sand	of Tar Sand	Water Phase After Fines Removed(1)	Relative(2) Fluorescence
Blank	-	1.7	0
Area B	8.3	6.2	93.0
Hole 11	4.3	3.6	128.7
Hole 21A	7.4	2.4	73.7
15-16-2 Top	6.8	1.6	25.0
15-16-2 Middle	7.9	4.6	50.9
15-16-2 Bottom	8.4	1.2	36.0
29-16-2 Top	7.4	1.6	46.1
29-16-2 Middle	7.6	1.8	35.2
29-16-2 Bottom	7.5	1.7	35.5
33-14-2 Top	7.9	2.0	40.0
33-14-2 Middle	7.9	1.9	45.0
33-14-2 Bottom	8.0	2.2	31.6

(1) Separated water phase from pot extractions were settled, decanted, acidified (to flocculate clays) and centrifuged (to remove solids).

(2) Relative fluorescence was measured on acidified solids-free water phase. Some soluble oil component may have been lost due to acidification, which springs oil, see Figure 8.

It was first noted that acid tar sands gave very clear water phases. However, treating tar sands with alkaline solutions resulted in a straw-brown colour in the range of 8-10 pH. At higher pH's above about 11 the colour was frequently so brown-black that zeta potential measurements could not be carried out.

The oil content of the water phase was measured by flocculating the suspended material at reduced pH's of less than 2, and recovering the oil from the precipitate by solvent extraction. Some results with different tar sands are plotted in Figure 2-10 for values of less than 0.2μ suspended oil. This size was below the minimum of suspended solid particles in alkaline water phases. Colloidal oil of less than 0.5μ is generally about 50% greater in amount than less than 0.2μ oil.

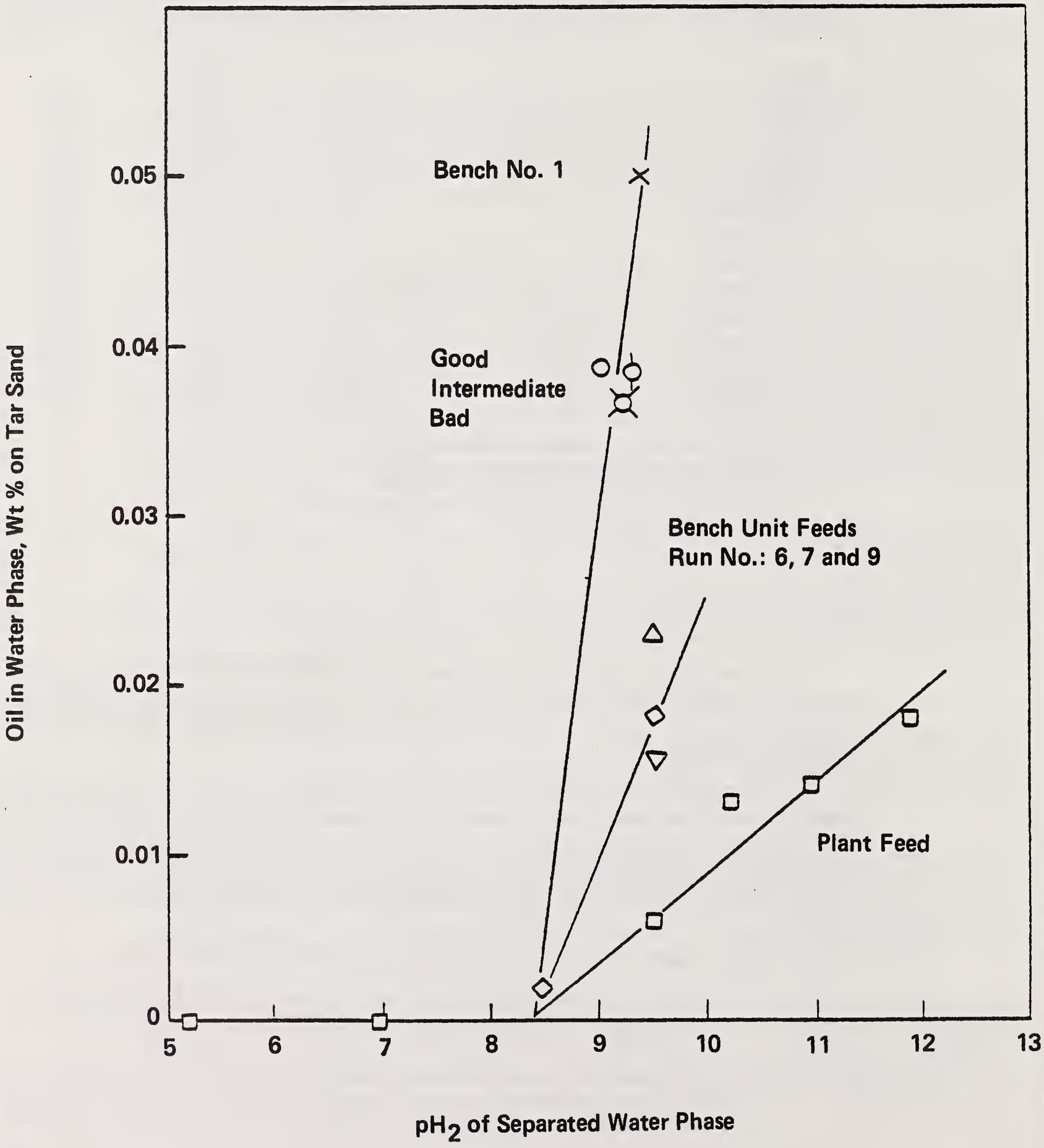
The eight tar sands evaluated in our studies may be classified into three groups:

- *(a) "Aged" tar sands, which includes Good, Intermediate, Bad and Bench No. 1*
- *(b) "Fresher" tar sands which includes Unit Feeds - Run No. 6, 7 and 9*
- *(c) "Plant Feed", which appeared to be distinctly different in giving lower values than even more recently received samples of "fresher" tar sands. It should be noted that this larger sample had been carefully stored under nitrogen at 40°F.*

A sharp increase in emulsified oil with increasing pH above a critical value of 8.3 was found in all cases. Oil emulsification with increasing pH is not unexpected, but it is interesting that this "critical" pH is almost identical with the natural pH of most good quality Beaver River tar sands. Essentially no oil was found in water phases from just straight separation of tar sands with water,

Figure 2-10

Effect of pH on the Amount of Dissolved, Micelle or Colloidal Oil Water Phase (< 0.2 μ)



although water soluble surfactants are probably present in amounts not detectable by the method used.

Further, if oil emulsification is a function of "aging",see Table 2-8, "oxidation" of organic as well as inorganic components of the tar sands may occur. If this is true, oxidation would presumably occur through autoxidation forming peroxides, which would be hydrolyzed to hydroxyl groups in the molecules of the oxidized portion of the oil. Infrared spectrographs on the N_2 dried extracted oil did indicate possible oxidation, Figure 2-11, that in addition to the carbonyl groups present, 5.7-5.9 microns, in the natural (acid) surfactants, observed before, there was also indication of hydroxyl (NH also occurs in this region) at 2.8-3.3 microns. This only tends to substantiate the possibility of hydroxyacids as the product of oxidation. Further evidence is required to show that appreciable oxidation does occur.

However, if oxidation of organics does occur, then the solubility of the oxidized portion of the oil would be expected to increase. Higher solubility would result in the formation of colloidal micelles when the C.M.C. (critical micelle concentration) was exceeded. The micelles would readily flocculate in acid media, due to reduction in zeta potential or surface charge. Our observations are, therefore, consistent with the speculation recorded above.

The maximum values of colloidal oil found dispersed in the water phase in these studies was about 0.7% on oil.

The results clearly indicate that aqueous-soluble oil components occur in the hot water flotation process. These interfacially active polar components play a role in the flotation extraction of oil, that will be discussed later in this report.

2-4 Solubility in Organic Solvents

Solubility studies were carried out to provide a basis for selecting practical hydrocarbon solvents that do not demonstrate incompatibility. Solubility parameters were used as they are a measure of the total cohesive energy holding a unit volume of liquid together and not merely the strength of a particular molecular bond. Measured solubility parameters were found to give an excellent correlation of behaviour, and an internal structure of the oil is postulated based on measured relative solubility parameters of separated oil components.

2-4-1 General Solvency

The oil from the Athabasca Oil Sands is a non-uniform size mixture of distinct chemical types, Figure 2-12. The Solvent Power of a solvent for the oil is a measure of compatibility, resulting from association forces between molecules of the solvent and those of the oil. For example, polar solvents have greater interattraction forces that do not permit compatibility with the non-polar or poorly hydrogen bonding hydrocarbons of the oil.

Literature solubility and hydrogen bonding parameters of pure solvents were found to correlate with visual oil solubility scaling tests, Figure 2-13. The data described distinct solubility zones, which are a function of temperature and solvent to oil ratio. Dipole moments did not show a distinct correlation with these solubility data.

In general, oil dissolved in low hydrogen bonding solvents with solubility parameters of less than 11, and greater than 7. As liquids that have similar solubility parameters are compatible, then the oil from the oil sands must have a solubility parameter in this range. Complete solubility was also obtained with some very high hydrogen bonding solvents. Solvents with intermediate and high hydrogen bonding parameters showed selective solubility effects of either asphaltene precipitation or partial solubility of the oil.

Most practical hydrocarbon solvents for commercial solvent dilution for solids and water contaminant removal have solubility parameters in the established solubility zone. Deasphalting solvents have low hydrogen bonding - low solubility parameters of <7. The amount of asphalt rejection increases with decreasing solubility parameter.

(a) Theory

In hydrocarbon solubility problems, the non-polar or weakly polar nature of the molecules enables more precise definition to be attained with theory and practical measurement. The free energy of mixing, equation 1, Table 2-10, is of prime importance as miscibility of two phases

Table 2-8

Oil Component of Water Phase(1)

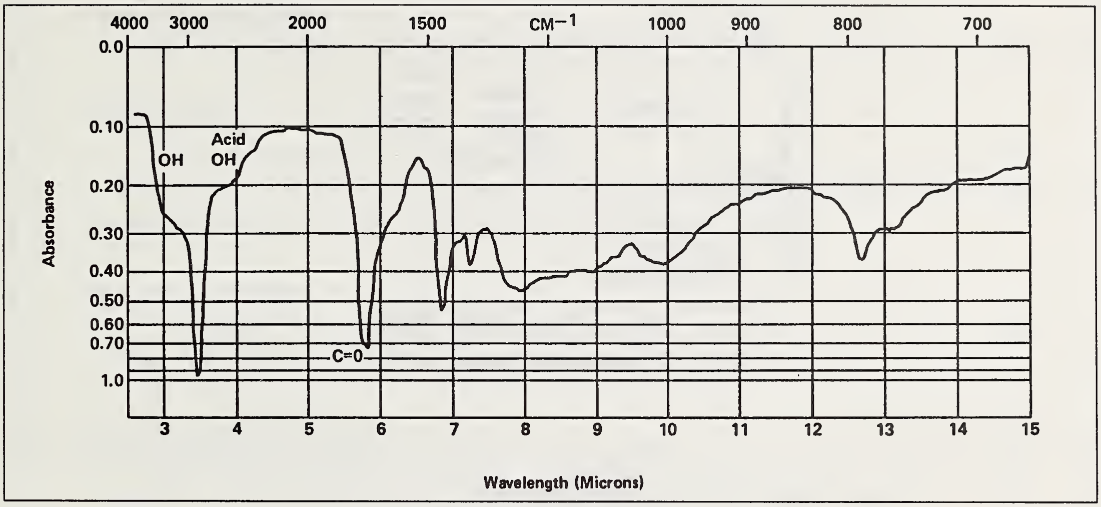
Sample Group	Beaver River Tar Sand (Designation)	Water Phase pH(2)	Water Phase Oil(3) Wt % On TS	Water Phase Oil(3) Wt % On Oil
A	Plant Feed	5.2	0.0000	0.000
	"	7.0	0.0000	0.000
	"	9.5	0.0059	0.059
	"	10.2	0.0128	0.128
	"	10.9	0.0140	0.140
	"	11.9	0.0179	0.179
B	Good	9.0	0.0386	0.364
	Intermediate	9.3	0.0377	0.401
	Bad	9.2	0.0366	0.654
	Bench No. 1	9.4	0.0499	0.475
C	Unit Feed-Run No. 6	8.5	0.0020	0.021
	" 6	9.5	0.0179	0.186
	" 7	9.5	0.0153	0.159
	" 9	9.5	0.0228	0.240

(1) Passing thru 0.2μ filter in "colloidal suspension"
(2) Of separation adjusted by NaOH addition to original tar sand slurry
(3) Obtained by procedure of acidification and solvent extraction of water phase

Figure 2-11

Infrared Analysis of Extracted Oil from Water

(From Intermediate Tar Sands)



occur only if the change is negative. This will occur at higher temperatures, and with a large entropy change which is always positive because of a more disordered mixture. Thus the heat of mixing or solution becomes important in determining the sign and magnitude of the free energy change.

Hildebrand proposed the heat of mixing relationship at constant volume shown in equation 2 where the square root of the internal pressure or cohesive energy density, i.e. $(\Delta E/V)^{1/2}$, is the solubility parameter δ. Scatchard, and Small, derived a relationship for a binary mixture, equation 4, from which solubility parameters of mixtures can be calculated, equations 4 and 5. However, these simple equations are difficult to apply to complex hydrocarbon mixtures without detailed composition and extensive solubility parameter data that is not readily available. Other methods for deriving solubility parameters, such as thermal coefficients, surface tension, critical pressure, or molar attraction constants, either are difficult to apply or give poor accuracy. Direct solubility measurements are best.

Although London's dispersion forces are prime contributors to the cohesive energy, dipole interactions and hydrogen bonding, equations 7 and 8, must also be considered. In the case of non-polar hydrocarbons these contributions are small and can be neglected without serious error. However, with polar solvents there is a significant effect of the hydrogen bonding power of the solvent on oil solubility.

2-4-2 Critical Solubility Point

In addition to the important factors of gravity and viscosity in the selection of a practical hydrocarbon solvent, solvent power as measured experimentally by solubility parameters is important in attaining good solvency in solvent dilution and avoiding incompatibility. Solubility parameters of complex refinery hydrocarbon mixtures that might be used in solvent dilution are not readily obtained, so a simple technique for their measurement and comparison was used based on incompatibility arising from the insolubility of the least soluble asphaltene components of the oil. This critical solubility point of asphaltenes was determined by titrating oil in solution with different solvents against a reference titrant, such as n-heptane, using microscopic observations of the precipitation end point.

Figure 2-12

A General Athabasca Oil Composition

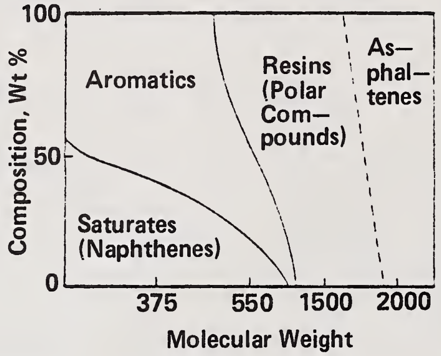
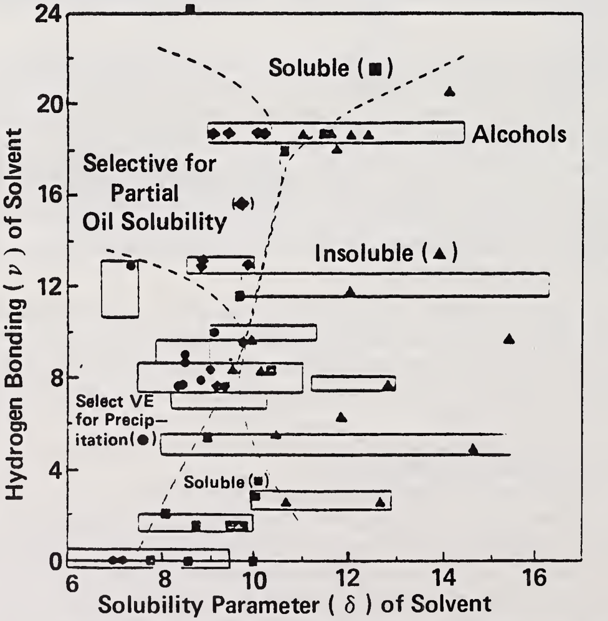


Figure 2-13

General Oil Solubility

(75 °F and 3/1 Solvent/Oil Ratio)



Note: Boxes refer to different classes of solvents
e.g. Alcohols

Table 2-9

Factor in Solubility Theory

Free Energy of Mixing

$\Delta F = \Delta H - T\Delta S$ .... (1)

Heat of Mixing

$\Delta H_M = V_M [(\Delta E_1/V_1)^{1/2} - (\Delta E_2/V_2)^{1/2}]f_1f_2$ .... (2)

Where ΔE is the energy of vapourization, V is the molar volume of components 1 and 2, V_M is the total volum, and f is the volume fractions of components 1 and 2.

Solubility Parameter

$\delta = (\Delta E/V)^{1/2}$ .... (3)

Where $\Delta E/V$ is the internal pressure or cohesive energy density.

Cohesive Energy Relation

$E_{MIX}^{1/2} (n_1V_1 + n_2V_2)^{1/2} = n_1(E_1V_1)^{1/2} + n_2(E_2V_2)^{1/2}$ .... (4)

Where E is the cohesive energy and n is the moles of liquid of V molar volume.

δ for a Mixture

Substituting in (4): $\delta 2 = (E/V)$ and x = mol fraction;

Then:

$\delta_{MIX} = \dfrac{x_1V_1\delta_1 + x_2V_2\delta_2}{x_1V_1 + x_2V_2}$ .... (5)

When the molar volumes are not significantly different

$\delta_{MIX} = x_1\delta_1 + x_2\delta_2$ or $\Sigma^n{}_1\, x_n\delta_n$ .... (6)

Dipole and Hydrogen Bonding

$E = E_L + E_D + E_H$ .... (7)

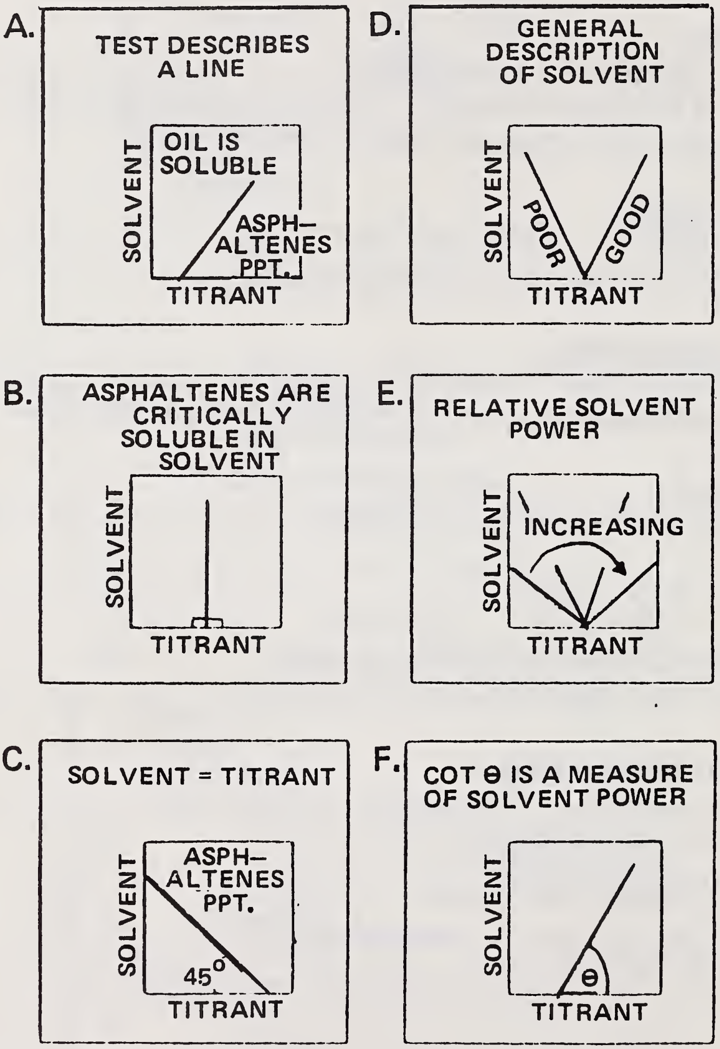
Where: E_L = London's Dispersion
E_D = Dipole Interaction
E_H = Hydrogen Bonding Contribution

Dividing by the molar volume V and substituting $\delta^2 = E/V$

$\delta^2 = \delta^2_L + \delta^2_D + \delta^2_H$ .... (8)

Figure 2-14

Interpretation of Solubility Results



The results of experiments expressed as volume of solvent per weight of oil and the volume of titrant per weight of oil, described a line as shown in Figure 2-14. If the slope of the line is positive, or in the first quadrant, it represents a good solvent Figure 2-14. If the line is vertical, Figure 2-14, the asphaltenes are critically soluble in the solvent. If the line has a negative slope, Figure 2-14, it represents a poor solvent. In this particular example, the solvent and titrant are the same, and hence the negative slope of the line is 45° with the x-axis. The description of a good solvent and a poor solvent, Figure 2-14, can be generalized to measure the relative solvent power, Figure 2-14. Thus, the slope of the line described for a given solvent-titrant system is a measure of the solvent power of the solvent. Cot θ will be shown to be a practical measure of the solvent power for hydrocarbon mixtures, Figure 2-14.

In obtaining the data, titrations were completed in less than 15 minutes. Standing of mixtures just before or after the end-point gave no change. Critical solvents, Figure 2-14, in amounts almost at the end-point in a few cases gave precipitation only after several days standing. Thus, the rate of flocculation was only found to be significant with these critical solvents. Further, too rapid titrant addition caused precipitation due to local high concentrations. This phenomenon was called surface flocculation, as it occurred at the temporary phase interface and dissolved with mixing. This was avoided experimentally by slow titrant addition and continuous mixing to maintain homogenity, particularly near the end-point.

Most of the experiments were carried out at 70°F temperature, and similar results were also obtained in some higher temperature experiments at 150°F. Thus for practical purposes application of relative 70°F solubility parameters to higher temperatures that might be used in a commercial solvent dilution process appeared valid.

As all the data plots obtained with different solvents were linear, this geometric relationship enabled a simple technique to be used for the prediction of the critical solubility of asphaltenes in other different titrant-solvent mixtures from a minimum of data. This technique requires extrapolation of the data to intercept on the y-axis, which is a fundamental parameter that characterizes the solvent, see Figures 2-15 and 2-16. Data transpositions can thus be effected as in Figure 2-17:

- establish a line for solvent A against titrant 1.
- extrapolate to intersect the y-axis.
- a value for titrant 2 is then determined and indicated on the x-axis.
- the transposition line can then be drawn between the intercept on y-axis and the value of the new titrant on the x-axis.

2-4-3 Specific Solvency

The results of experiments with a number of pure hydrocarbons are shown in Figure 2-18. It will be noted that in general the Solvent Power is a function of hydrocarbon molecular structure. The order of increasing solvent power from this data is paraffins<olefins<-naphthenes<naphthene<cyclo-olefins<condensed naphthenes<aromatics<condensed aromatics. Greater dispersion forces and hence higher solution energies of aromatics result in their superior Solvent Power for the Athabasca oil. Similar results were obtained with some more polar type solvents, Figure 2-19. Partial moments through chlorine substitution are responsible for the good solvent powers of the chlorinated solvents. These were found to be at least equivalent to aromatic and condensed aromatic hydrocarbon solvents.

The results with various typical complex refinery hydrocarbon mixtures such as varsol, virgin and coked gas oils have been plotted in Figure 2-20. It can be seen that similar results and trends in hydrocarbon compositon with solubility were found. For example, deodourized varsol, essentially a paraffinic mixture, has a low solvent power and could be used for deasphalting. Whereas cracked and particularly aromatic gas oils are good solvents. Similar directional results were obtained with deodourized varsol as the reference titrant, Figure 2-21.

Figure 2-15

Y-Axis Intercept Is Characteristic of a Particular Solvent

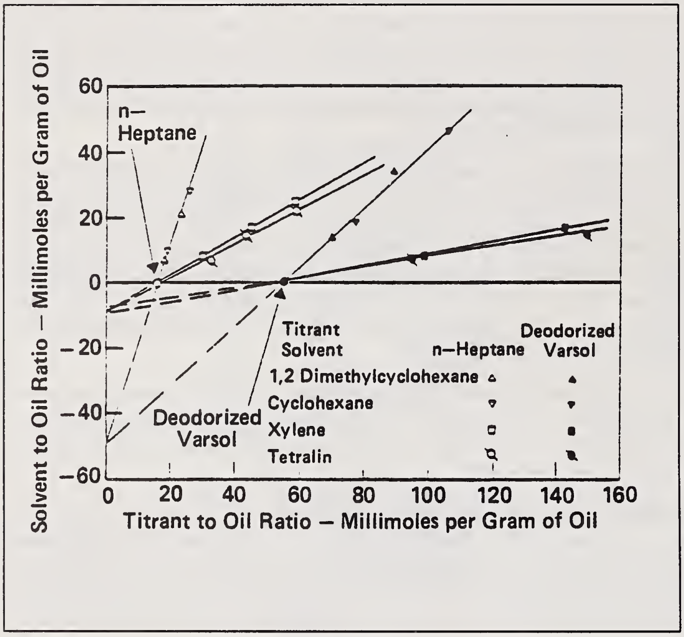


Figure 2-16

Y-Axis Intercept Is Characteristic of a Particular Sol-

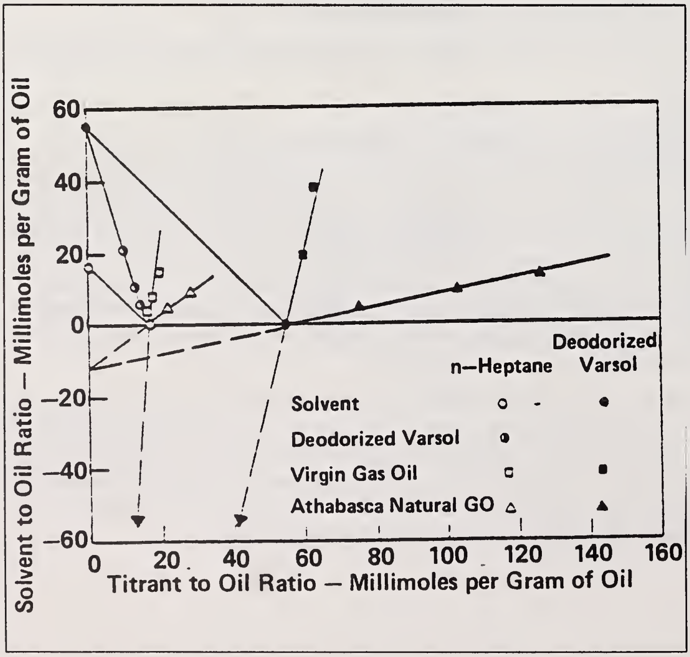


Figure 2-17

Solvent Transposition Procedure

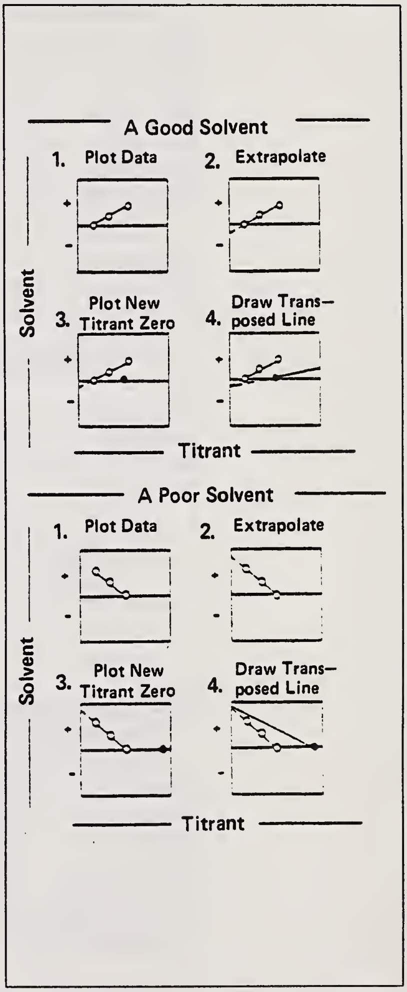


Figure 2-18

Pure Hydrocarbons

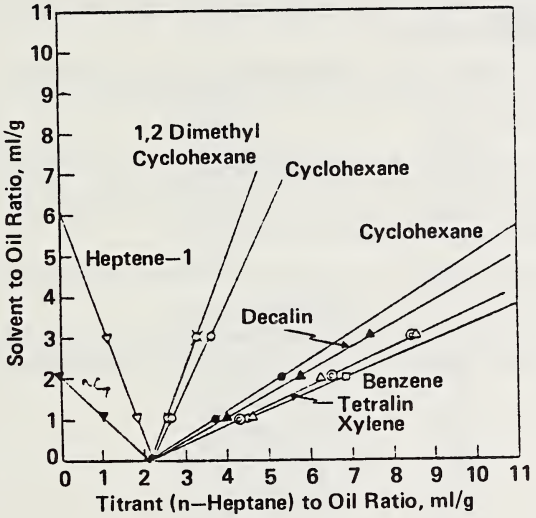


Figure 2-20

Typical Refinery Hydrocarbon Mixtures

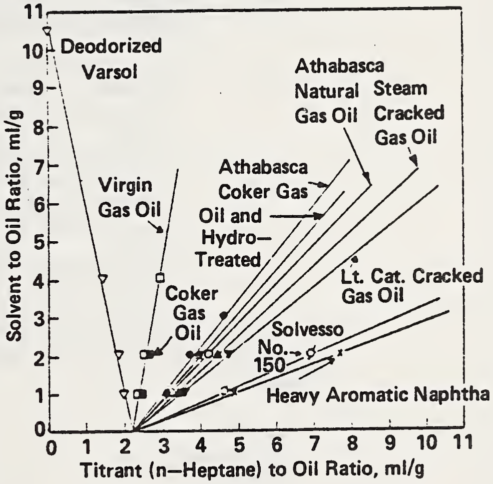


Figure 2-19

More Polar Solvents

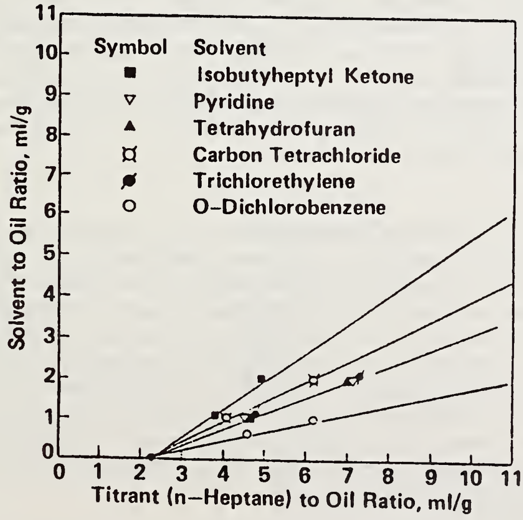
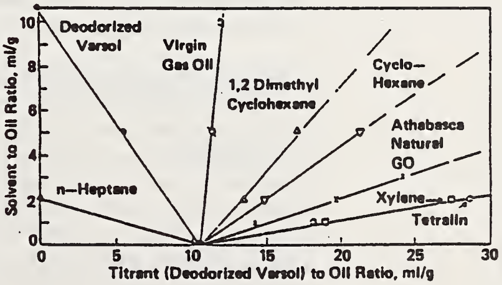


Figure 2-21

Hydrocarbons Relative to Deodorized Varsol



2-4-4 Solvent Solubility Parameters

A practical solubility parameter- Cot θ, Figure 2-14F, was selected as the value best suited to characterize the solvent for the oil relative to n-heptance titrant. The basis for selecting this molar (Cot θ) or volume (Cot θ_v) solubility parameter was:

- *(a) The values of Cot* θ different quadrants are a mirror image above and below the x-axis. The significance of Cot θ thus becomes apparent after considering the transposition data already presented.
- *(b) A good solvent has a positive value. If the solvent is a very good solvent the line will lie close to the x-axis, which has a value of +00. The line for a poorer solvent will lie closer to the y-axis.*
- *(c) A poor solvent has a negative value. By definition the titrant has a value of -1 in that the angle with the x-axis is 135o . Solvents with values greater than -1 will be relatively poorer solvents than the titrant. Whereas solvents with values between 0 and -1 will be better solvents than the titrant.*
- *(d) Solvents in which asphaltenes are just critically soluble have values of θ = 90, and Cot θ = 0, as described by a vertical line.*

Just at the critical solubility point a change in the interfacial tension between the immiscible phases from zero to a positive value occurs. Similarly, Cot θ is zero at the critical solubility point and hence

$$\sum_{x=1}^{x=n} \mathrm{Cot}\,\theta^{x}\, m_{x} = 0,$$

where m is the mole fraction of one of x solvent components in the system. Using this equation which is similar in form to the Gibbs-Duhem in thermodynamics, Cot θ predictions for various solvent mixtures were calculated and shown to be in agreement with experimental results.

Measured Cot θ solubility parameters are summarized and compared with literature δ values in Table 2-10. A general correlation exists, which is restricted to low hydrogen bonding hydrocarbon solvents that exhibit solubility parameters of less than 10, Figures 2-22. Polar solvents like pyridine and ketone do not fit the correlation line. However the technique developed for the measurement of Cot θ solubility parameters can be readily used to approximate δ solubility parameters of typical commercially available hydrocarbon mixtures. Low boiling aromatic solvents are more effective at lower mixing efficiency, Figure 2-23. Interfacial tension was also found to be generally related to relative solubility parameters, Figure 2-24. Coked gas oil was found to be an excellent solvent for solids and water removal.

2-4-5 Oil Component Solvency

The composition of oil in terms of the amounts of saturates, (naphthenes), aromatics, resins (polar compounds), and asphaltenes, Table 2-4, is dependent upon the method used to carry out the separation. The solubility parameters of separated oil fractions, obtained using relative adsorptions on silica gel and attapulgus clay in different solvents, have been measured. Separation with only silica gel gave solubility lines close to that for deasphalted oil, Figure 2-25. A much superior separation into more distinct fractions was obtained with a silica gel-attapulgus clay system, as shown by comparison with Figure 2-26. Thus the technique of measuring relative solvent power also provides an analytical tool for evaluating the efficiency of component separation as well as providing some fundamental measure of the nature of the component. It should be noted that the solubility parameter of oil less asphaltenes, is a mean value, substantiating the additive properties of these solubility parameter measurements.

The effect of asphaltene concentration in the oil was studied to verify that it was indeed independent of the measured solvent power. The results are plotted in Figure 2-27. It can be seen,

Table 2-10

Solubility Paramete Summary and Comparison

Solubility Parameter	Cot θv	Cot θ	Hildebrand δ	Symbol
	Measured		(Literature)	
Pure Hydrocarbons				
n-Heptane	-1.00	-1.00	7.4	○
Heptene-1	-0.35	-	-	-
Cyclohexane	+0.48	+0.35	8.2	○
1,2 Dimethylcyclohexane	+0.38	-	-	-
Xylene	+2.14	+1.73	8.8	○
Benzene	+2.38	+1.38	9.2	○
Decalin	+1.79	-	-	-
Tetralin	+2.14	+1.96	9.5	○
Hydrocarbon Mixtures				
Deodourized Varsol	-0.21	-	-	-
Coker Gas Oil	+0.18	-	-	-
Virgin Gas Oil	+0.18	-	-	-
Athabasca Coker Gas Oil	+0.82	-	-	-
Hydrotreated A.C.G.O.	+0.91	-	-	-
Athabasca Natural Gas Oil	+0.99	-	-	-
Steam Cracked Gas Oil	+1.12	-	-	-
Lt Cat. Cracked Gas Oil	+1.28	-	-	-
Solvesso +150	+2.37	+2.41	8.5	○
Heavy Aromatic Naphtha	+2.75	-	-	-
Other Pure Solvents				
Isobutyl Heptyl Keton	+1.41	+0.80	7.8	◇
Pyridine	+2.41	+1.30	10.7	□
Tetrahydrofuran	+2.41	-	-	-
Carbon Tetrachloride	+1.94	+1.19	8.6	●
Trichlorethylene	+2.41	+1.46	9.3	●
o-Dichlorobenzene	+4.13	+2.90	10.0	●

Figure 2-22

Solubility Parameter Correlation Exists Only for Non-Polar or Weakly Polar Solvents

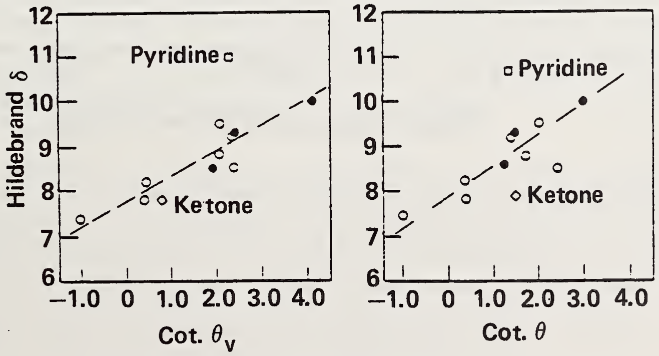
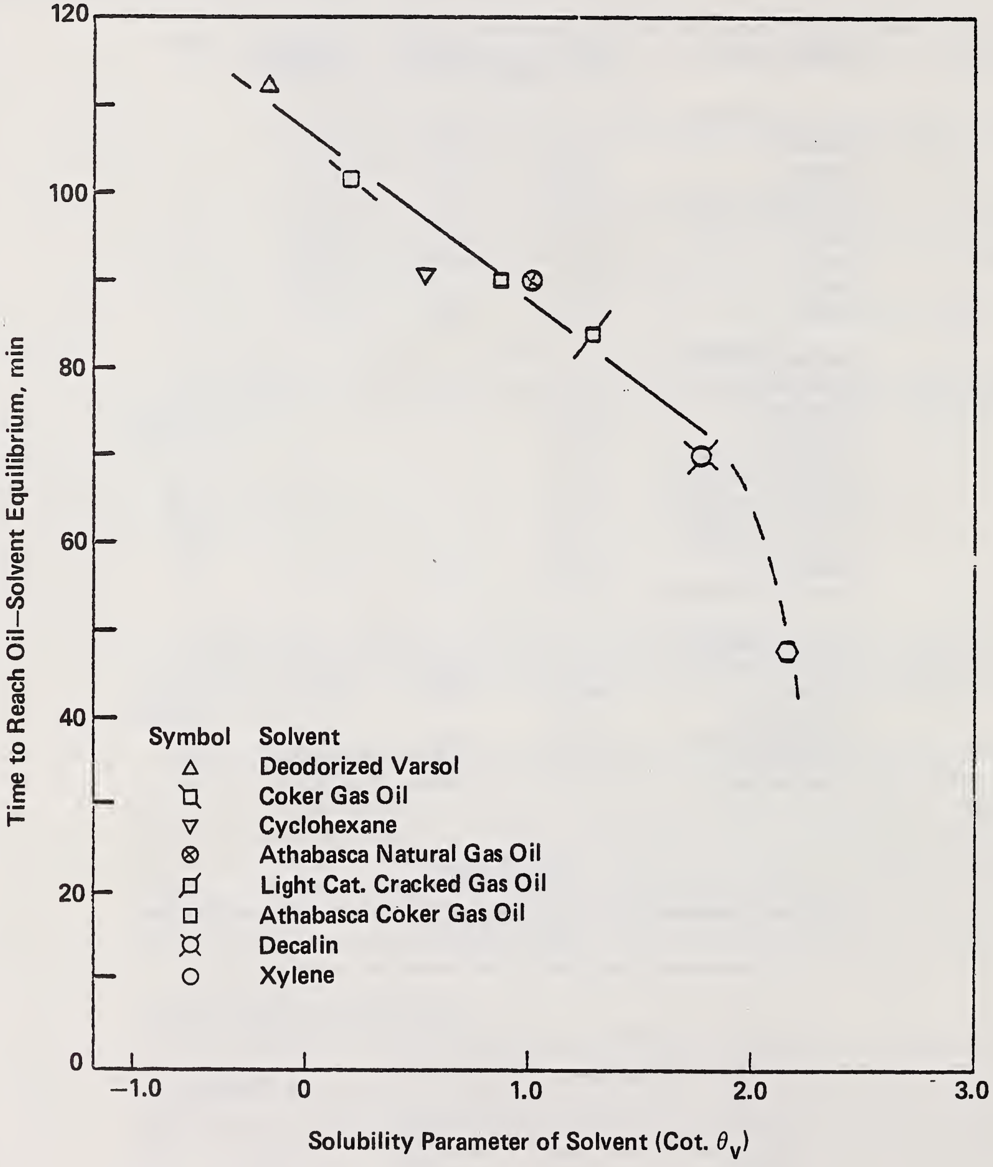


Figure 2-23

Low Boiling Aromatics Are Better Solvents at Low Mixing Efficiency



that as expected the concentration of asphaltene in the oil (less asphaltenes) does not affect the measured value of 2.4 ml n-heptane per g of oil within experimental error. Coincidentally, this is equivalent to Cot $\theta v = 2.4$.

Small solubility parameter differences in oils extracted from oil sands along the Athabasca river were found. For example, a 7.2° API oil gave a solvent ratio of 2.1 compared to 2.4 for the 8.3° API oil discussed above. However, other 8.0-8.5° API oils gave values as low as 1.6 and showed no correlation with typical physical properties. The larger the positive Cot θ for the oil the more peptizing power for asphaltenes. Thus the solubility power of the oil fraction is an important variable in solvency. Values of Cot θ_v obtained for the separated oil components are shown in Table 2-12.

2-5 Oil Structure

Our general knowledge of the oil from the Athabasca tar sands is that it is not only a mixture of small and large hydrocarbon type molecules, (isogel), but it is also composed of classes of distinct chemical types (heterogel), again of non-uniform size. These ranges of size and chemical types vary widely even within the general classes of components as discussed above. The oil, therefore, may be regarded as a mixture of isogels. Although it may also be classified as a heterogel, because of the different chemical species present; and an isosol at high temperatures, where the oil behaves more like a simple liquid, the solubility behaviour of the oil is also characteristic of a colloidal system.

The solubility parameters of oil components can provide some understanding of the internal structure of the oil as well as its behaviour toward deasphalting solvents. The higher the value of the solubility parameters or Cot θ_v of a component then the greater its "solubilizing power" for asphaltenes. Thus, components of higher solvent power in the oil will constitute the first environment around the asphaltene nucleus. Lower solubilizing power components will be farther away from the nucleus. The order of components in the asphaltene micelle will, therefore, be in decreasing order of "solubilizing power", i.e. asphaltene-polar resins-less polar resins-aromatics-saturates (naphthenes-paraffins) as shown in Table 2-12.

The values of hydrogen to carbon atomic ratio do not entirely substantiate the micelle structure proposed by Kruyt, i.e. asphaltenes - high molecular weight (aromatic) - low molecular weight (aromatics) - compounds of particularly aliphatic character - compounds of strong aliphatic character - compounds of complete aliphatic character. The increasing amount of heteroatoms, particularly nitrogen, with increasing solvent power for asphaltenes suggest that the solubilized micelle is more one of increasing molecular polarity as the center of the nucleus is approached. This is also substantiated by positive zeta potentials of the oil components in nitropropane, which shows increasing polarizability of the components with the order shown for the micelle.

The oil micelle is therefore one of high polarity, as asphaltenes contain metals such as vanadium (vanadyl) and nickel in their structure, to lower polarity and lower cohesive energy density and lower molecular weight resins, together solubilized in an oily saturated naphthenic environment by aromatics. Thus the micelles are individually structured by weak intermolecular attraction and repulsion forces between weakly-polarized hydrocarbons, with some strong polar forces at the center. As attraction forces generally increase with increasing size, the association forces decrease with the distance from the center of the micelle. Further, at lower temperatures interattraction forces between micelles can form micelle chains with interlocking into three dimensional networks and resulting in increased viscosity until eventually a plastic-solid structure is attained.

The process of oil solution in a hydrocarbon solvent therefore proceeds toward the nucleus of the asphaltene micelle. Saturates dissolve first. Then aromatic components on the periphery of the micelle, that are held by the weakest association forces, dissolve next. With further solvent addition, further layers are removed from the dispersed micelle. The energy required to overcome the association forces in the micelle structure is supplied by the solution energy of the solvent. Paraffins have the least amount of solution energy, enough to denude the micelle centers, but insufficient to effect solvation and overcome the strong cohesive forces acting between nuclei, which result in flocculation and precipitation of the asphaltenes at solvent to oil ratios that increase with increasing molecular weight of the solvent.

Figure 2-24

Relationship of Interfacial Tension and Solvent Power

(Moles n-Heptane/Toluene in 2 Volumes of Solvent

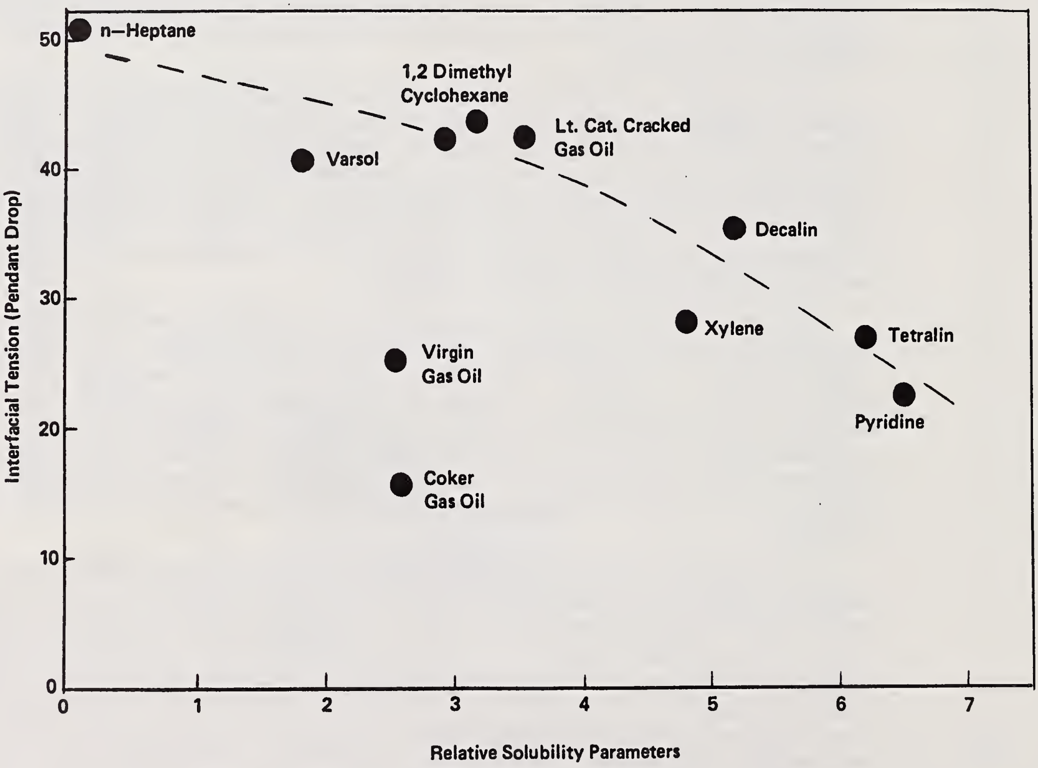


Figure 2-25

Silica Gel Separation

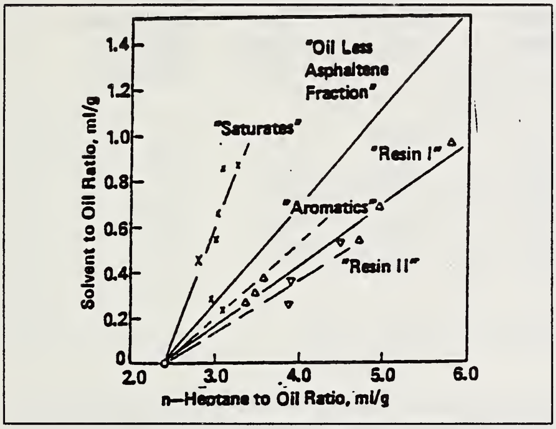


Figure 2-26

Attapulgus Clay & Silica Gel Separation

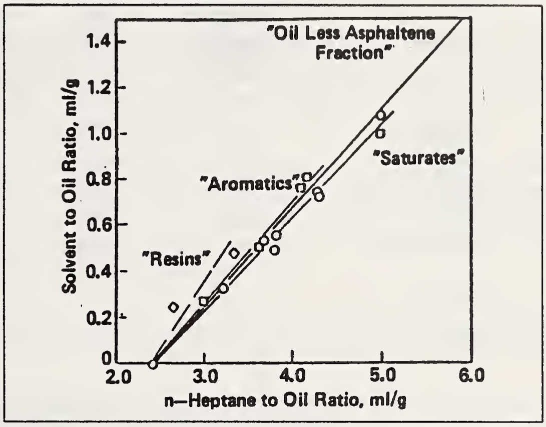


Figure 2-27

Asphaltene Concentration Effect

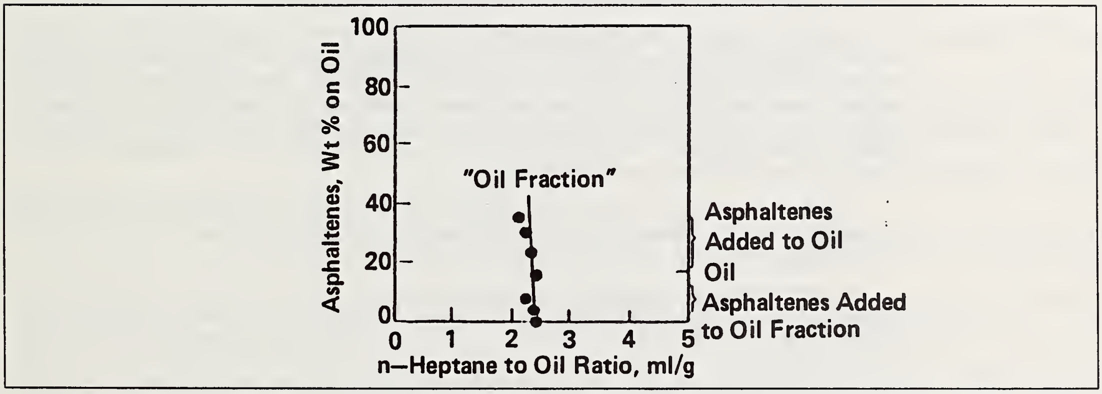


Table 2-11

Oil Component Solubility Parameters

Oil Component	Cot θv (from Fig. 5-2)
Saturates	1.1
Aromatics	3.2
Resins I	4.0
Resins II (More polar)	4.5
Oil Less Asphaltenes	2.4

Table 2-12

Oil Component Order in Oil Micelle Structure

Oil Fraction	Solubility Parameter Cot θv	H/C Ratio	Sulphur Wt %	Nitrogen Wt %	---------Relative-------- Zeta Potential (mv)	Approximate Number of Molecules
Saturates	1.1	1.65	1.9	<0.02	-7.4	6
Aromatics	3.2	1.38	5.9	0.2	-17.0	8.5
Resin 1	4.0	1.53	5.4	0.7	-26.1	2
Resin 2*	4.5	1.46	5.1	0.9	-30.0	0.5
Asphaltene	-	1.23	8.2	1.2	+15.6	1

* More polar

It has been found that the surface of oil particles contain predominantly anionic groups; e.g. carboxylic acid groups, in contact with the aqueous phase. Surfactants with these groups are negatively charged due to dissociation. The degree of dissociation will be a function of pH. Positive ions, however, will be restrained by the electrostatic negative attraction in the aqueous phase, hence creating a double layer. Polyvalent ions can be restrained in the form of salts.

The dissociation of anionic surface groups is dependent on pH, and dissociation constants can be obtained. The zeta potential is small in acid solution, if the groups are of moderate strength, like naphthenic acids, and large in alkaline solution, since dissociation and higher charge is promoted; i.e. R-COO-. The dissociation should increase gradually from acidic conditions to alkaline conditions. Double layer theory would predict it goes through a maximum, if other ions were constant. If salt addition is used to attain these higher pH's, the effect of counterions would also tend to create a maximum.

In fact, the experience curve of zeta potential of oil particles versus pH of the water phase increases from acid to a maximum in alkaline conditions at ~9 pH, consistent with the explanation of ionization of carboxylic to carboxylate species (see Section 10).

In considering, the structure of the bitumen in the oil sands, an internal organization appeared to exist that may have an interesting feature. The argument can be developed as follows. The electrophoretic mobility of separated asphaltenes from the tar sands in nitropropane dielectric constant of about 20, has been measured to be positive (1.0μ sec/volt/cm). In water dielectric constant of about 80, the electrophoretic mobility of asphaltenes has been measured to be negative (1.4μ sec/volt/cm). Using the principle that the phase having the higher dielectric constant generally acquires a positive charge, then it may be deduced that the dielectric constant of asphaltenes will be between 20-80. As most hydrocarbons, e.g. saturates, aromatics, lubricating oils, etc, have dielectric constants between 2-5, then asphaltenes in oil will most probably carry a positive charge. If asphaltenes or its micelles are sufficiently close to the bitumen/water interface to exert a charge influence, then this is of scientific interest as presently the double layer theory of interfaces does not recognize an internal surface charge.

If the effect of an internal positive charge from asphaltenes at the interface but in the bitumen phase is influential, it could in practise maintain more ionized carboxylic anions at the interface in acid media that would result in higher zeta potentials at lower pH. This is observed experimentally (see Section 10-2-3), and hence might be an explanation for the shape of the curve.

In summary, the micelle structure for bitumen, proposed on the basis of solubility parameters/nitrogen polarity/zeta potential measurements, is an ordered system with predictable solubility behaviour.

2-6 SUMMARY

Some of the findings that relate to oil sand separation, particulalry by hot water flotation, are listed below for conveience:

- The bulk of the oil, 98-99 wt %, in the tar sands is soluble in aromatic solvents, e.g. , benzene.
- The 1-2 wt % of the total oil not soluble in benzene, is particularly soluble in polar solvents such as acetone and pyridine chlorocompounds. The pyridine soluble hydrocarbons are at least partially soluble in sodium hydroxide. Ethanol has been found to be a selective solvent for surface active polar hydrocarbons.
- The polar hydrocarbons that are not extracted with benzene, are: (a) adsorbed on the solids in the tar sands; (b) go into aqueous solution especially under alkaline conditions and at high temperatures; (c) form films at the interface of oil-water; (d) are extracted with ethanol; have very similar infrared spectra and appear to be carboxylic acid polar hydrocarbon components from the resins fraction of the oil.
- Oils extracted with benzene from different tar sands have shown some significant quality differences, particularly in gravity, viscosity, and amounts of highly polar hydrocarbons.
- A linear gravity-viscosity relationship at 210°F for these different oils was established.
- The high gravity-viscosity constant and the steep viscosity-temperature relationship found for these oils are characteristic of high aromatic hydrocarbon content. This is substantiated by direct measurements of oil constituents.
- It has been shown that an approximately linear relative density relationship for water and oil exists over the range of temperature 120-210°F.
- The sulphur, nitrogen and oxygen (by difference) contents of saturate, aromatic, resin and asphaltene components of the oil increase in the order of the components shown.
- Iron and nickel contents of the oil are about 66 ppm, however the vanadium content is about 5-6 times greater.
- The ash from nearly completely solids-free oils have also shown that appreciable quantities of titanium, zirconium calcium and iron are present.
- Aqueous soluble oil components have been found in all systems of oil in contact with an aqueous phase, e.g. , the water phase from hot water flotation separations.
- The solubility of the polar hydrocarbons in aqueous media have been found to increase (a) with increasing temperature, (b) with increasing amounts of highly polar hydrocarbons in the oil, and (c) markedly at high and at low pHs.
- The soluble oil also changes the pH of the contacting solution. The net effect is that the oil behaves as an amphoteric, i.e. , an acid in alkaline media and a base in acid solution.Thus, the addition of pH controllers are affected by the solubility of the oil (and vice versa) as well as being adsorbed by clay minerals, as well as determine the amount of surfactants in the water phase that are available to make hot water flotation work..
- The fluorescence of soluble acid-oil components generated in alkaline solutions is essentially constant with decreasing pH. Fluorescence of the soluble base-oil component in acidic media decreases with increasing pH. This indicates the presence of two entirely different soluble oil components.
- These two main types of naturally occurring polar hydrocarbons have been isolated. The base soluble oil component appears to be primarily a carboxylic acid. The acid soluble oil component is probably a nitrogen sulphur heterocyclic with acid and basic functional groupings e.g. resin, porphyrin, etc.

3

MINERALS

The minerals were originally studied by others as a geological formation but now may be regarded as important both to an understanding of the mechanism of hot water flotation as well as offering future possible byproducts, e.g. zircon, of a commercial venture. Further, the surface properties of the minerals that contaminate the bitumen product streams need to be removed in separation. Hence, mineral characterization studies were directed toward these specific objectives, and involved examination of many different solids samples extruded from the Mildred Beare oil sands. However, because of the emphasis placed on minor to trace amounts of the minerals present in oil sands, a perspective should be maintained on the significance of the detailed discussion on each mineral.

The bulk of the solids were found to be silica, silicates, aluminum-silicates, and oxides, that are relatively inert materials and hence they have very little, if any, chemical effect in the separation process. However, small quantities of some materials such as carbonates, sulphides, and heavy minerals can significantly affect tar sand processability. The interaction of ions, such as Ca^{++}, Mg^{++}, Fe^{+++} etc., with clay minerals is also an important factor in separation. Thus, a study of minerals should involve not only the separation, identification, but also physical and chemical properties. Some exploratory experiments have been carried out to learn a little of the role of these minerals. The different types of minerals observed in the experimental samples are summarized in Table 3-1. The amount of occurrence, however, varies from essentially the bulk of the sample in the case of a quartz sand to isolated grains of some of the rare heavy minerals.

A mineral is defined as a substance occurring in nature with a characteristic chemical composition and usually possessing a definite crystalline structure. Minerals are classified on the basis of their chemical composition, crystalographic form, hardness, and gravity. These properties are inter-related and used in their identification. Minerals can also be classified according to their flotation properties. In the ensuing discussion of the minerals in the oil sands, classifications are organized according to physical, chemical and flotation properties. The usual terminol-

Table 3-1

Minerals in the Oil Sands

A. **Light Minerals** (~99% of total minerals)

1. Quartz (SiO_2) is the most abundant (~60-90+%)
2. Clay Minerals: Kaolinite [$Al_4(Si_4O_{10})(OH)_8$] and illite (variable*)
3. Feldspar (small content with quartz)
4. Mica: muscovite [$KAl_2(AlSi_3O_{10})(OH)_2$], sericite
   biotite [$K(Mg, Fe)_3(AlSi_3O_{10})(OH)_2$], chlorite [$Mg_3(Si_4O_{10})(OH)_2\text{-}Mg_3(OH)_8$]
5. Carbonates: siderite ($FeCO_3$), dolomite [$CaMg(CO_3)_2$], calcite $(CaCO_3)_2$
   magnesite ($MgCO_3$) etc (variable)
6. Chalcedony: grains observed in larger mesh fractions

B. **Heavy Minerals**: >2.96 g/m (% of total minerals)

1. **Majors**

(a) Oxides: Titanium - leucoxene and limenite ($FeTiO_3$)
Iron - hematite (Fe_2O_3), magnetite (Fe_3O_4) and limonite [$FeO(OH)nH_2O$]
(b) Silicates: Tourmaline [$XY_3Al_6(BO_3)_3(Si_6O_{18})(OH)_4$], zircon ($ZrSiO_4$),
epidote [$Ca_2(Al, Fe)Al_2O(SiO_4)(Si_2O_7)(OH)$] and
staurolite [$Fe_2Al_9O_7(SiO_4)_4(OH)$]
(c) Sulphides: Pyrites (FeS_2), and Sphalerite (ZnS) morcosite
(d) Carbonates: Siderite ($FeCO_3$)

2. **Minors**

(a) Oxides: Corundum (Al_2O_3), cassiterite (SnO_2) and Rutile (TiO_2)
(b) Silicates: Garnet [$A_3B_2(SiO_4)_3$], Kyanite (Al_2SiO_5),
Chloritoid [$(Fe,Mg)_2(Al_4Si_2O_{10})(OH)_4$], Zoisite [$Ca_2Al_3(SiO_4)_3(OH)$],
amphiboles, pyroxenes, sillimanite (Al_2SiO_5), spinel ($MgAl_2O_4$)
(c) Sulphides: Chalcopyrite ($CuFeS_2$), Bornite (Cu_5FeS_4)
(d) Carbonates: Dolomite [$CaMg(CO_3)_2$], calcite ($CaCO_3$),
(Magnesite and rhodochnosite ($MnCO_3$) in mixed carbonates)

3. **Possible Minerals Present**

Uraninite (UO_2) or carnotite [$K_2(UO_2)_2(UO_4)_2.nH_2O$], apatite [$Ca_5(F,Cl,OH)(PO_4)_3$],
sphene [$CaTiO(SiO_4)$], pentlandite [$(Fe,Ni)_9S_8$], pyrrhotite ($Fe_{1-x}S$),
cordierite [$Mg_2Al_3(AlSi_5O_{18})$], molybdenite (MOS_2), manganite [$MnO(OH)$],
pyrolusite (MnO_2), psilomelane [$BaMn''Mn^{4}8O_{16}(OH)_4$]

---

* (2K, 2Na, Ca)O; 3.33 (Mg, Mn)O; 4.3 $(Ae, Fe, Ti)_2O_3$; 16 $(Si, Ae)O_2$; $4H_2O$ or 1.3 $(K, Na)_2O$; 0.6 (Mg, Fe)O; 3.3 $(fe, Ae)_2O_3$; 16$(Si, Ae)O_2$; $5H_2O$

ogy of non-opaque, (transparent or translucent) and opaque (not transmitting light), as applied to minerals, have also been used. Another classification that has been adopted is a general group system into which the minerals could be arranged on the basis of their chemical structure, i.e. oxides, silicates, sulphides, carbonates and others.

The individual minerals have been discussed to describe some of the characteristics and variations in habit and appearance that occur. Identification using the criteria of colour, crystal structure, appearance in either reflected or transmitted or polarized light, streak, gravity, chemical composition, reaction to chemicals, as well as X-ray diffraction and emission spectrographic analysis have been the basis of assignment of names to the grains observed. The wide variety of sizes, shapes, forms, crystal habits, types of minerals, and variations due to significant weathering once impurities particularly adsorbed on the surface almost precludes any fundamental studies in the laboratory utilized pure components as worthwhile. Pure mineral results are only directionally applicable to the expected behaviour of the minerals in the tar sands, provided there is no major surface contamination.

The bulk of the suite of minerals are very similar to those of common sediments or clastic deposits which appears to have undergone appreciable weathering. Thus, the bulk of the minerals may be regarded as rather an inert group of minerals. However, there are very small amounts of some minerals, namely, carbonates and sulphides, that determine the natural pH of the water phase, and are more readily oxidized to effect changes in pH. Further, the fine division of some minerals, e.g. SiO_2, results in some solubility that increases the salt content of the water phase and can affect interfacial behaviour.

In general, the minerals vary appreciably with location, both in type and in amount. A general trend observed is that both carbonates and sulphides appear to occur more at the bottom of the formation. This may be due in part to their reaction and removal into solution from the solids at the top part of the exposed formation adjacent to the Athabasca river.

The minerals, however, would be expected to vary widely both vertically and horizontally in the formation. As it is a sedimentary deposit, local concentrations of heavy minerals may occur, which are fairly non-existent in other locations. It is assumed that these occurrences would tend to be more uniform horizontally within the formation than vertically. Our findings indicate some general trends, which may be fortuitous, and should be explored further.

3-1 Total Solids

A typical set of tar sand solids that represent the area are 12 characterization samples from the Escarpment area and 4 samples from the Beaver Creek area designated as proposed plant feed, good, intermediate and bad (see Tables 1-2 and 1-4). The latter samples are designated on the basis of processability. Of all these samples, the greatest emphasis was placed upon the Beaver Creek plant tar sand feed solids, as it presumably is more representative of the tar sands for the initial period of a future commercial operation. Description has been generalized on the basis of microscopies counts using sizing eyepieces of several samples separated by gravity fractionations and cemented in plastic discs for repeatable evaluations.

The total mineral suite in the tar sands is comprised of about 99% of light minerals, such as sand and clay minerals, Table 3-1. Small amounts of heavy minerals (>2.963 g/ml) also occur in all the tar sand samples studied. The light minerals are described in the first part of this section and were separated from heavy minerals by tetrabromoethane, i.e. 2.963 g/ml. The identification of light minerals was not rigorous and was mainly carried out after separation using microscopic observations. Heavier minerals are described in greater detail in the second part of this section as their identification and properties were the main object of this study to establish the potential for economic recovery of byproduct minerals.

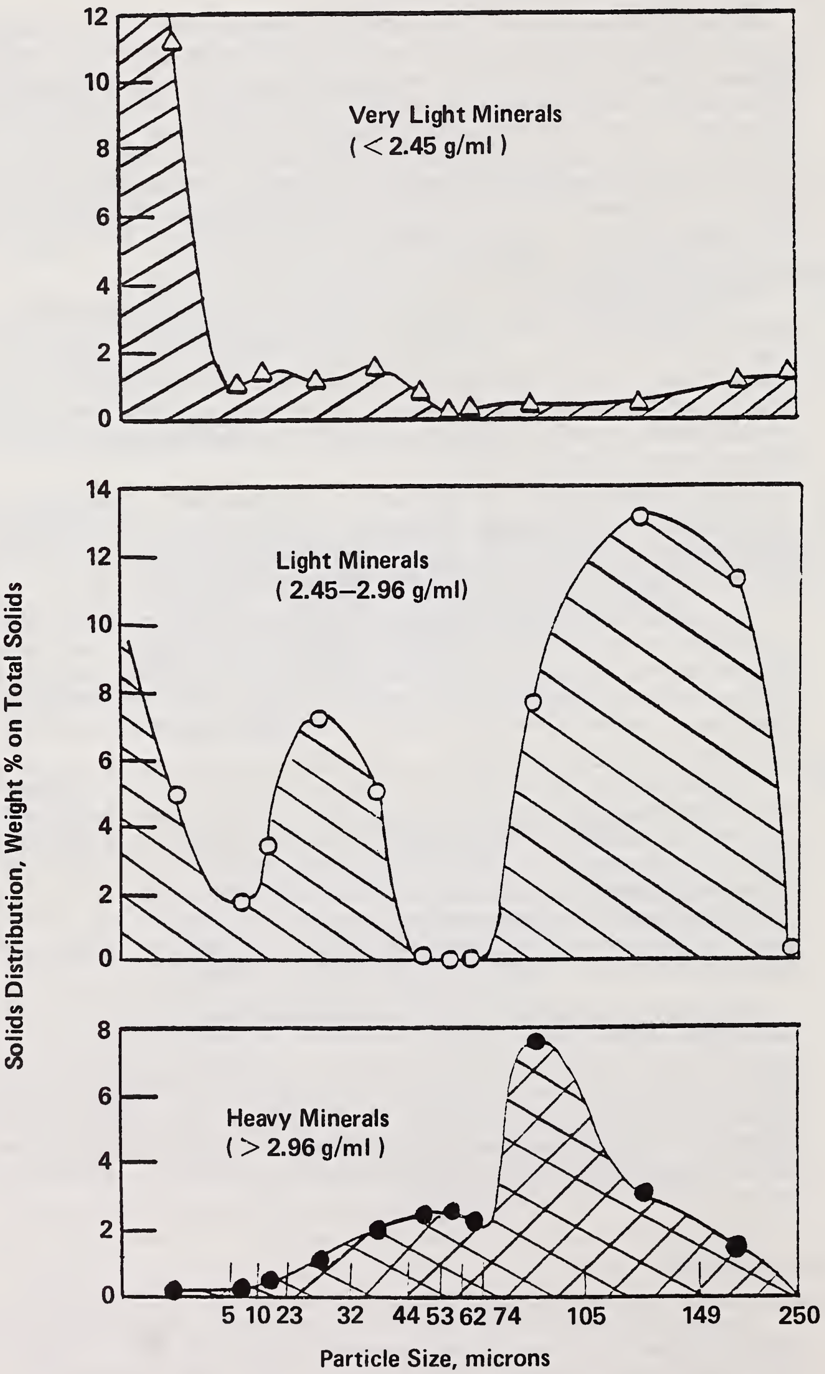
An example of the mineral size and density distribution is given in Figure 3-1 for Beaver Creek minerals.

3-2 Light Minerals

These minerals are mainly fine grained quartz sand together with lesser amounts of hydrous aluminum-silicate clay minerals, mainly weathered kaolinite and illite, see Figure 1-2. Other light minerals present, amounting to only 1 or 2% for Beaver Creek-Mildred Lake samples, are

Figure 3-1

Solids Distribution as a Function of Size and Density (Beaver Creek Solids)



feldspar and members of the mica and chlorite groups of minerals. However, feldspar can become predominate in some oil sand areas. The observed occurrence of these minerals is consistent with the occurrence of the accessory heavy mineral suite that will be discussed.

Only a very general description of the light minerals is given. This description, based on many microscopic observations of a number of sands from different tar sands, point out that the size, form, physical, chemical, structure and hence surface properties of the minerals vary widely. Any fundamental studies of solids should take into account these different aspects, and results will give only directional ideas as to what is actually happening in a practical process. The bulk of the sand in most tar sands studied is readily separated from oil with water, which is consistent with the fact that silica is hydrophilic, particularly in mildly alkaline media and is water wet in the formation, see Section 10.

3-2-1 Sand

(a) Size

The bulk of the sand is about 30-200 U.S. mesh in size for most of the samples measured. The particle size distribution of three extracted sand samples is shown in Figure 3-2, and also for twelve characterization samples in Table 3-2. The wide differences in size distribution have also been observed by most workers in the field. The significance of size distribution is its relationship to bitumen saturation in that large grained samples generally have higher bitumen saturations.

Also shown in Table 3-2 are ash analyses on the different fractions. The purpose of these ash measurements was to determine correction factors for use in early processability studies. It is interesting to note, from the plots of these data that the ash values of the solids from different tar sands are quite variable. Presumably, the differences may reflect quantities of material present with the sand, e.g. amphorous silica, carbonates and silicates as well as carbonaceous materials. Calculated total ash from these separations matched very closely the measured total ash of the sample.

(b) Shape

Sand, the most abundant mineral in the Beaver Creek-Mildred Lake oil sands, was found to comprise 70-90 wt% of the total oil sand samples studied, Table 3-2. The sand is mainly α quartz (SiO_2), identified by X-ray diffraction patterns, and has a specific gravity of about 2.65 g/ml. It occurs as a clastic type, i.e. unconsolidated grains in which the crystals are no longer distinct. A few well-formed crystals have been observed in our microscopic studies. These appeared to have the habit of the trigonal trapezohedral type of the hexagonal class. Most of the sand grains, however, are tapered or elongated and have sharp ends. Some crystals are twisted and bent while others are smooth. Twining is frequent even to the point of large aggregates of well formed crystals very compact and intimately intergrown or cemented together by silica.

The most common deviations occur in the larger grain sizes; i.e.greater than about 40 mesh. Many of these larger grains show inclusions of various colours such as yellow, red, white, and black and some are milky in appearance. Colourless inclusions of either liquid or gas have also been observed. Abrasion, etching, and pores, are more frequent in these larger crystals. However, all these defects observed have also been found in the smaller grain sizes to a lesser extent. Most of the sand occurs in the size range of 10 to 325 mesh. The grains are very irregular, often acute, and conchoidal fractures are common. Some grains are smooth and rounded, presumably from attrition in water. In transmitted light most crystals exhibit a splendid transparency or vitreous luster. Generally only when crystals have inclusions or are abraded are the quartz grains not translucent, but this occurs to only a small extent (<5% of the sand).

A cryptocrystalline form of quartz has also been observed in all tar sands studied. This very fine grained crystalline form of quartz appears very angular (chip-like) under the microscope.it presumably is the material that other investigators have referred to as "chert".

Interbedding (quartz aggregation through silicification) or orthoquartzite does not occur to any large extent, and has been estimated to be probably less than one percent of the total minerals. The formation of aggregates or sandstone is more common and involves quartz grains cemented together with certain types of other minerals other than silica. (This will be discussed again later).

Figure 3-2

Sand Size Distribution

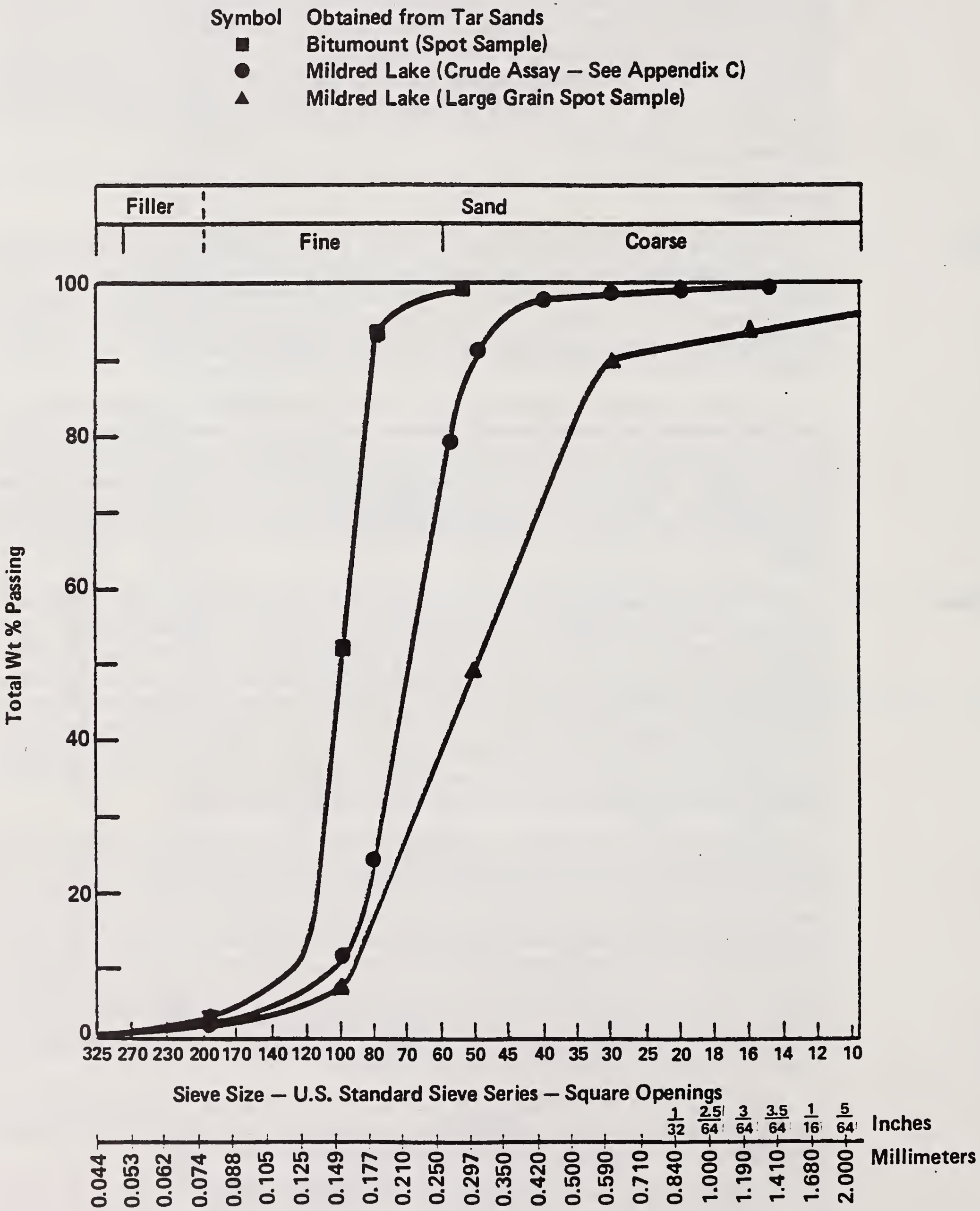


Table 3-2

Inspections on Tar Sand Characterization Samples and Extracted Solids

Core Number	Area B	Hole 11	Hole 21A	15-16-2			29-16-2			33-14-2		
Depth	-	-	-	Top	Middle	Bottom	Top	Middle	Bottom	Top	Middle	Bottom
Footage	-	-	-	67-99	115-163	163-214	32-63	63-110	110-174	79-110	110-159	174-206
Inspections on Solids												
Distribution, Wt %												
20+ U.S. Mesh	9.9	0.1	0.2	0.5	0.6	0.3	0.0	0.1	10.6	0.1	0.5	0.4
20-60 " "	53.6	7.8	2.6	11.7	3.6	7.5	18.2	26.2	39.3	11.7	10.9	32.0
60-100 " "	20.5	58.5	23.9	22.6	15.6	49.8	64.5	41.6	28.2	46.7	34.8	32.2
100-140 " "	4.8	14.0	29.2	17.4	16.3	10.6	7.4	9.2	9.0	13.2	15.0	6.0
140-200 " "	2.9	3.9	15.3	10.6	16.7	4.6	2.1	4.4	3.5	6.8	7.2	2.9
200-325 " "	2.2	3.1	7.6	8.7	8.5	4.7	1.3	3.3	2.9	4.4	7.1	3.4
325- " "	6.1	12.6	21.2	28.5	38.7	22.5	6.6	15.2	6.5	17.1	24.5	23.0
Ash on Solid Wt % (1)												
20+ U.S. Mesh	98.93	-	-	-	-	-	-	-	99.25	-	-	-
20-60 " "	99.73	98.97	92.49	96.91	99.52	97.12	99.36	99.39	99.57	98.98	97.34	99.55
60-100 " "	99.70	99.63	98.85	98.48	99.31	99.17	99.66	99.60	99.67	99.54	99.09	99.24
100-140 " "	99.62	99.55	99.27	98.80	99.61	99.17	99.61	99.48	99.42	99.50	99.10	99.22
140-200 " "..	99.23	99.08	99.01	97.58	99.04	98.90	99.24	98.99	99.14	99.15	98.44	97.99
200-325 " "	98.13	97.97	98.33	94.16	97.76	97.70	98.36	97.63	97.99	98.20	97.17	96.58
325- " "	89.01	93.60	89.67	92.02	93.12	90.44	90.11	89.59	89.75	91.46	92.32	90.91
Total (Calculated)	**98.94**	**98.74**	**96.84**	**96.04**	**95.79**	**97.24**	**98.95**	**98.00**	**98.86**	**98.00**	**97.09**	**97.30**
Total (Measured) (4)	**98.96**	**98.58**	**97.16**	**96.02**	**95.75**	**97.23**	**98.94**	**97.80**	**99.03**	**98.08**	**96.94**	**97.72**
Surface Area of 5μ less (2)												
M^2/gm	11.1	-	6.2	1.7	11.9	7.4	12.0	5.2	9.9	3.0	9.8	14.2

(1) Extracted with benzene, acetone and pyridine.
(2) By Perkin-Elmer Sorptometer. Samples contained pyridine soluble oil.

3-2-2 Clay

Besides being a generic term for specific minerals, clay also implies particle size. "Clay" is frequently defined as material less than 325 U.S. mesh ($<44\mu$) in size. This term is mainly for practical convenience in the laboratory that is interchangeable with "fines". It includes not only clay minerals present in the tar sands, but "chert" or finely grained crystallined quartz, and silts. The bulk of the "fines" is, however, comprised of clay minerals (e.g. Kaolinite $Al_4(OH)_8 Si_4O_{10}$ and illite-variable composition) with some silica. The "fines" comprises from 1 to 30 wt% of the total tar sands. It has averaged about 15 wt% of the particular samples studied, and appears to be weathered, e.g. low surface area of $<5\mu$ (Table 3-2), that would result in only surface adsorption of polyvalent ions and naturally occurring surfactants, but exhibit no adsorption in the clay mineral lattice that can occur with well formed minerals.

(a) Clay Minerals

In the particular samples studied, the clay minerals are essentially kaolinite and illite types. These clay minerals occur with appreciable quantities of absorbed iron. Illite, which is the more acid clay mineral, can contain considerably more absorbed iron than kaolinite. Both these clays are normally white when pure, but occur in shades of grey to brown in the tar sands. These colours have been generated in these pure clay minerals merely be absorbing different amounts of iron as determined in our clay adsorption studies. The colour of the clay is, therefore, an indication of the degree of iron absorption. This is particularly evident after ashing, and samples can be graded by the depth of the characteristic red colour of iron.

Kaolinite is a hydrous aluminum-silicate generally occurring in hexagonal-shaped plates. It is derived by the alternation of other aluminum-silicates, particularly feldspar, and therefore occurs with this mineral. Illite is a mica-like clay belonging to the hydrous mica mineral family. Illite differs from mica in that it contains less alumina in its structure, and a higher water content, and potassium is frequently replaced by calcium and magnesium. Not too much information is present in the literature on the adsorption and capacity of these clay minerals for substitution of metal ions that can be applied directly to the tar sand materials. This information and particularly rates at which ions are exchanged, would be quite important to a better understanding of the hot water separation process. It might be noted here that clay minerals have gravities from 2.2 to 2.6 g/ml. However the gravity of these minerals in the tar sands may in part be increased by adsorbed metals.

(b) Fines

The fines in the tar sands exist in two forms. First, as pockets or strata in the formation which readily disperse in water and are probably almost completely water-wet in the natural state. Very little oil appears to be associated with the samples of fines from this source which have been used in our studies, except for water soluble polar compounds that have migrated into these strata. Second, fines are distributed through the tar sand structure, presumably to some extent in the water films, although very small nodules of clay can exist in what appears to be homogeneous tar sands. This is evidenced by small nodules of clay observed after Soxhlet extraction of the oil and drying of solids. Some of the clay distributed through the structure is presumably partially oil-wet and this clay can have significance in the hot water separation process. Suspensions of fines result in very rapid settling of a bulk of the solids, most of the remaining solids settle out in 12-24 hours. This was sometimes due to the fact that the original oil sand had "aged". However, some fine materials have remained in stable suspension for many months verifying that part of the fines are either colloidal in size and/or highly surface charged. The degree of dispersion varies widely in different samples and is a function of pH and salts present. These dispersed solids are a major barrier to recycle of water in hot water extraction.

(c) 5μ and Less

Assuming that Stokes Law is obeyed by irregular clay mineral particles, the settling velocity of 5 material or less was calculated to be 0.85 cm per hour in an aqueous suspension of fines. Suspensions of fines from different tar sands, obtained by mixing tar sands with water and filtering through a 325 mesh US Screen Sieve, were settled for periods of about six hours. The supernatant liquid that contained 5 material suspended was then withdrawn by means of a hypodermic syringe. The water was evaporated almost to dryness and the solids were washed with acetone, benzene, acetone, pyridine, acetone, water and dried in an oven. These oil-free materials were submitted for differential thermal analysis, Figures 3-3 (a) to (d), and X-ray to determine the clay minerals present.

The differential thermal analysis patterns obtained on 5μ or less of some standard clays, Figure 3-3, are compared with analysis of tar sand clays, Figure 3-4. The general patterns of the clay show that only illite and kaolinite or halloysite are the main constituents. This has been observed by others. These are crystal structures and although the lattice is ordered (X-ray analysis), it does not follow that these clays are uniform in the chemical composition of the lattice unit. Bentonite and montmorillinite are not present.

The exothermic peaks at 980°C for the tar sand samples are small and diffused. It has been reported in the literature that particularly ferrous iron, associated with kaolinite reduces this peak. Further, the slow exothermic reaction taking place in all 12 characterization samples between 100 and 400°C is not due to the loss of water and hydration, but is probably due to reaction taking place in the material. A similar pattern has been observed with pure illite and kaolin treated with ferric chloride, although the pattern in this case was not as pronounced. Ferric chloride treatment also results in a colour change from white to grey, particularly with illite. The amount of iron present in the sample has an effect on the DTA pattern. These points together with the fact that it is a mixture of clay minerals makes the interpretation of these preliminary DTA studies difficult. Additional X-ray analyses on similar samples, Table 3-3, substantiated these findings and indicated variable quantities of fine silica in the samples, particularly Hole 11,

Figure 3-3 (a)

Differential Thermal Analysis Patterns on 5µ and Less Material from Area B, Holes 11 and 21A

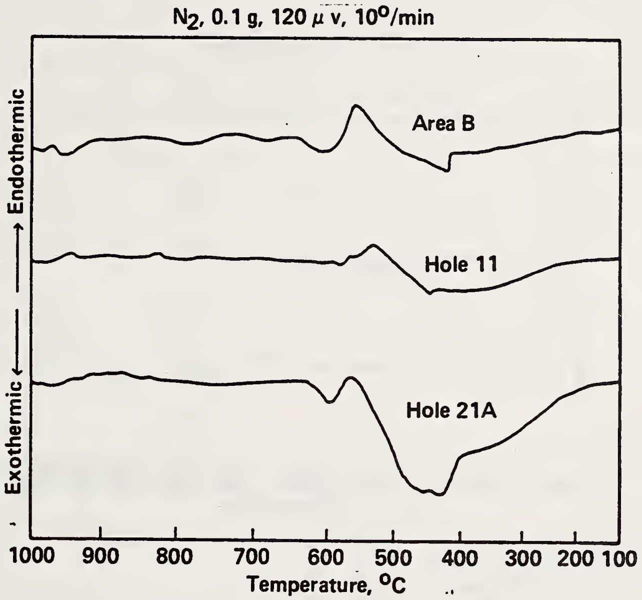


Figure 3-3 (b)

Differential Thermal Analysis Patterns on 5µ and Less Material From Core Hole 15-16-2

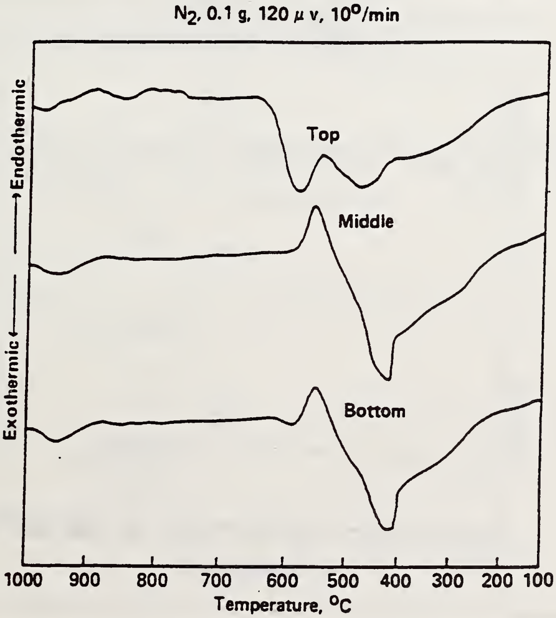


Figure 3-3 (c)

Differential Thermal Analysis Patterns on 5µ and Less Material From Core Hole 29-16-2

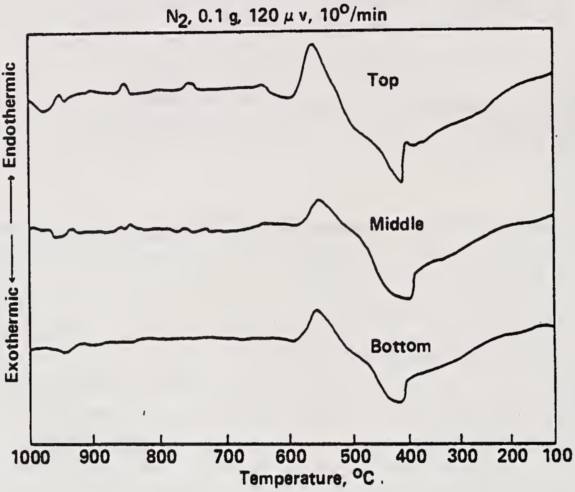


Figure 3-3 (d)

Differential Thermal Analysis Patterns on 5µ and Less Material From Core Hole 33-14-2

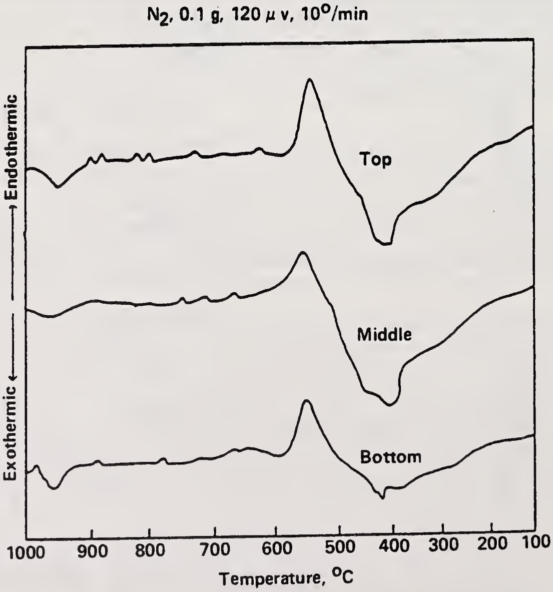


Figure 3-4

Differential Thermal Analysis Patterns for Some Reference Clay Samples

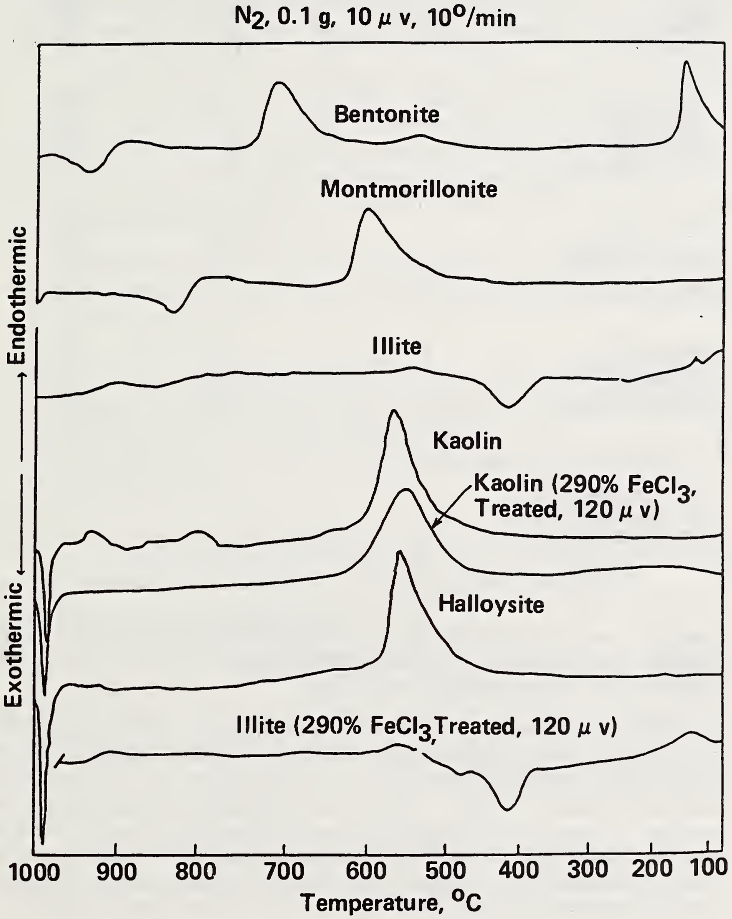


Table 3-3

X-Ray Diffraction of Clays

Clay From	% Illite (1)	% Kaolinite (2)	% Quartz (3)
Area B	8	74	18
Hole 11	9	35	56
Hole 21A	16	59	25
15-16-2 Top	10	52	37
15-16-2 Middle	28	65	7
15-16-2 Bottom	26	67	7
29-16-2 Top	14	74	12
29-16-2 Middle	18	63	19
29-16-2 Bottom	12	80	8
33-14-2 Top	17	74	9
33-14-2 Middle	23	74	3
33-14-2 Bottom	23	68	9

(1) Illite, based on d = 10.
(2) Kaolinite, based on d = 7.2.
(3) α Quartz, based on d = 1.82.

Hole 21A, and 15-16-2 Top, all of which exhibit poor processability. The ratio of illite to kaolinite varied widely, 2.6-9.2. There did not appear to be any obvious correlation of the clay mineral ratio with processability, see Section 7.

It is interesting to note that the parent tar sands of each of the samples that show a regular illite, kaolinite patterns processed well in hot water flotation separation. The two samples which showed poorer processability were 15-16-2 Top and Hole 11. The former exhibited an exothermic peak at about 580-590°C. This peak was quite sharp suggesting this was not due to the presence of a specific hydrocarbon and was not identified. However, there were no unusual α spacings in the X-ray. This peak has once been observed in DTA analyses on other fines samples. In the case of Hole 11, the pattern is very weak indicating that there is appreciable dilution by other material, i.e. silica (chert).

Although it was thought that DTA would give a better evaluation of the clay minerals together with X-ray, these preliminary data do not substantiate the original approach used. However, this technique can be used conveniently to check if swelling clays e.g. bentonite and montmorillinite are present, as the types of clays are detrimental in the hot water flotation process.

3-2-3 Other Light Minerals

Only isolated crystals of feldspar have been observed in most of the sand samples studied. No attempt has been made to isolate and identify these minerals. However, they appear to be of the variety of orthoclase ($KAlSi_3O_8$), which has been reported by other investigators in the mineral field of the tar sands. The degree of occurrence, however, is very small, estimated at less than 1%, in most of the samples inspected under the microscope. Some crystals were fairly well-formed, while others appear to have undergone weathering and are smoky in appearance.it is interesting to note that many of the other accessory minerals that will be discussed later in this report can be derived as alteration products of feldspar. However, it can be a main component of oil sands from other locations.

Mica occurs in the tar sands to less than about 1%. The crystals are usually hexagonal and can be seen readily by their ability to reflect light from samples of separated minerals. Most of the mica occurs in the gravity fraction of 2.7 to 3.1, and appears to be muscovite ($KAl_2(OH)_2AlSi_3O_{10}$). The mica is split into exceedingly thin transparent sheets, which have a vitreous to silky or pearly luster. It might be noted here that mica occurs frequently with accessory minerals, such as garnet, staurolite, kyanite, sillimanite, epidote and hornblend(3).

There is another variety of mica which has been observed to exist and has been called "sericite". This is usually the product of alteration of feldspar. The term sericite has been assigned to this mineral on the basis that it readily breaks down into minute scales which have a silky luster, and in turn the plates readily break down under mild stress into minute particles. This forms a very finely divided white mica which might be confused with quartz chert in appearance. The amount of chert (SiO_2) and "sericite" (aluminum-silicate) present in the "clay" can be readily determined by X-ray.

Biotite ($K(Mg, Fe)_3(OH)_2AlSi_3O_{10}$) has also been observed as isolated grains in the tar sand samples studied. It occurs in thin black sheets, sometimes dark brown and pearly, which exhibit a splendent luster.

It may also be mentioned here that only infrequently has chlorite ($Mg_3(Si_4O_{10})(OH)_2\,Mg_3(OH)_6$) been observed to occur in the lighter fractions of the heavier minerals in a pseudo-hexagonal, tabular transparent crystalline form which are coloured green. It is similar in habit to the crystals of the mica group, but not a member. It is not foliated and occurs as thicker flakes or scales. It exhibits a vitreous pearly luster and appears in the gravity fractions of 2.6-2.9 g/ml.

3-3 Heavy Minerals

As a major objective was to identify potential mineral byproducts from an oil sand recovery project, heavy mineral occurrence and properties were emphasized.

3-3-1 Historical Background

The first mention found in the literature of heavy minerals, such as zircon, in the tar sand was made 20 years ago by Clark (1944). Since that time the most noteworthy studies of mineral types have been made by Mellon, 1956, and Carrigy, 1959, 1963. These studies were concerned primarily with deducing the genesis of the tar sands, and dealt mainly with the non-opaque minerals, Table 3-4. Boyd and Montgomery discussed minerals very briefly, as their main objective was to describe the oil. Other workers have reported the heavy mineral presence in coarse grained McMurray sands from 1-12 wt%.

There is considerable divergence in the relative proportions of heavy minerals reported by previous investigators, Table 3-4. For example, Carrigy found an abundance of pink garnet in the coarse grained samples that he studied, whereas Mellon reported garnet to be present in very small quantities in most of his samples. Hence, the first step taken to define the mineral suite was a review of the literature data that revealed some points of concern. For the purpose of discussion all the information reported has been summarized in Table 3-5.

- *(a) The total amount of heavy minerals, that is both opaque and non-opaque portions, are not reported with two exceptions.*
- *(b) The two total heavy mineral percentages quoted were very high (6.4 and 15.8%) and were attributed to the presence of large amounts of siderite ($FeCO_3$), but in these cases as in many others no ratio of opaque to non-opaque were recorded.*
- *(c) No identification or quantities of opaque minerals were given.*
- *(d) The samples on which this work was carried out were obtained from outcroppings and cores located along about 50 miles of the Athabasca River as illustrated in Figure 3-5.*

Table 3-4

Heavy Minerals reported in Literature on Athabasca Tar Sands Reference

Mineral Type	Clark(1) (1944)	Kupsch(2) (1954)	Mellon(3) (1956)	Boyd-(4) Montgomery (1961)	Carrigy(5) (1963)
Non Opaque					
Tourmaline	X	X	X		X
Zircon	X	X	X	X	X
Rutile	X	X	X	X	X
Garnet	X	X	X		X
Staurolite		X	X		X
Kyanite	X	X	X		X
Chloritoid			X		X
Apatite		X	X		X
Amphiboles		X	X		
Sillimanite		X	X		
Biotite		X			
Muscovite		X			
Spinel	X				
Epidote			X		
Sphene			X		
Zoisite			X		
Magnesite				X	
Dolomite				X	
Opaque					
Ilmenite	X				
Pyrite	X				
Siderite					X
Comundun				X	
Hematite			X	X	
Limonite			X		
Magnetite			X		

(1) Clark, K.A., *Hot-Water Separation of Alberta Bituminous Sand*, The Canadian Institute of Mining and Metallurgy Transactions, Vol. XLVII, 1944, p. 257.

(2) Kupsch, W.O., *Bituminous Sands in Till of the Peter Pond Lake Area Saskatchewan*, Saskatchewan Dept. Mineral Resources, Report No. 12 (1954).

(3) Mellon, G.B., *Heavy Minerals of the McMurray Formation*, from Geology of the McMurray Formation, Part II Research Council of Alberta, Report No. 72 (1956).

(4) Boyd, M.L., Montgomery D.S., *A study of the Athabasca Bitumen from the Athabasca Quarry Mines Branch Report*, R-78, (Nov. 1961).

(5) Carrigy, M.A., *Petrology of Coarse-Grained Sands in the Lower Part of the McMurray Formation*, Research Council of Alberta, Information Series No. 45, (1963)/

Table 3-5

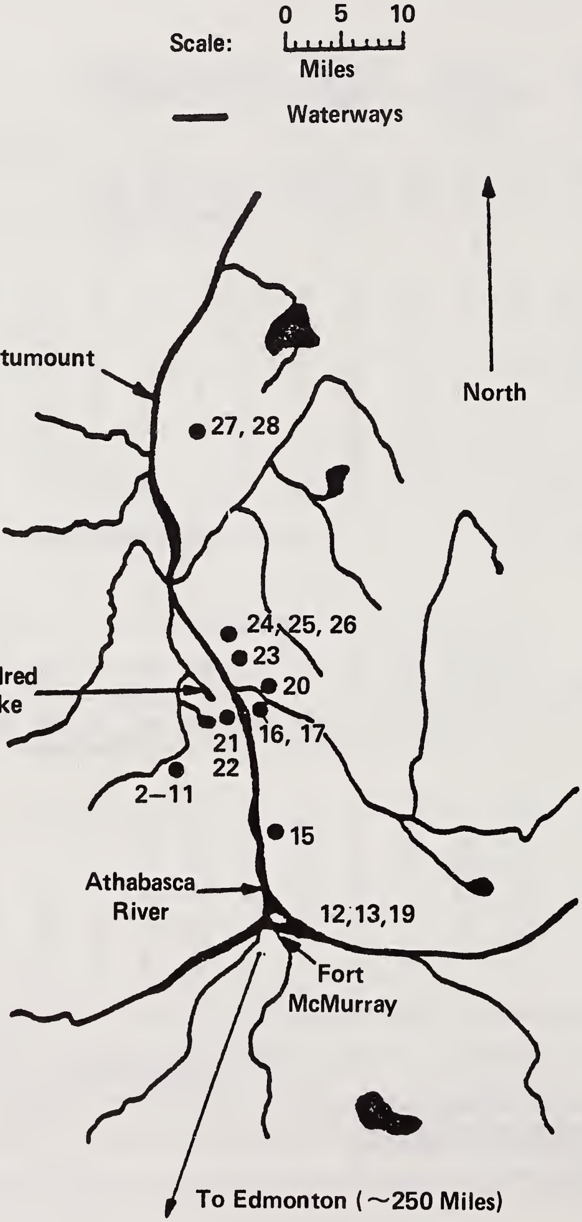
Summary of Existing Analyses of Tar Sand Heavy Minerals

Reference	Kupsch(2)	Mellon(3)														
Sample Number(a)(b)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Type	outcrop	Core										Outcrop				
Depth, ft		95	115	132	152	175	194	217	235	252	262					
Heavy Mineral, wt %	No Reference															
1) Non Opaque(c)																
Tourmaline	45	18	50	55	48	54	54	60	60	58	54	47	55	54	50	48
Zircon	13	3	9	5	9	1	6	4	8	8	13	8	3	9	21	11
Rutile	3.5	0	tr	0	0	tr	0	0	1	0	tr	3	1	1	1	2
Garnet	3.5	52	14	4	6	3	2	8	7	3	4	5	6	4	8	6
Staurolite	8	5	8	12	11	3	5	12	8	11	15	9	9	14	9	18
Kyanite	3	4	6	6	3	3	4	5	3	6	8	3	4	2	8	4
Chloritoid	11	5	10	17	18	35	27	6	9	12	5	25	21	14	2	10
Apatite	0	11	2	0	2	1	1	1	1	tr	1	0	0	1	0	tr
Amphiboles	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2) Opaque	80	Up to 80% of total heavy minerals														

Reference	Carrigy(5)											
Sample Number(a)(b)	17	18	19	20	21	22	23	24	25	26	27	28
Type outcrop					Core							
Depth, ft					157	160	128	89	97	105	255	305
Heavy Mineral, wt %				6.4	15.8	No References						
1) Non Opaque(c)												
Tourmaline	28	10	40	9	14	14	38	37	15	30	41	22
Zircon	15	41	20	16	12	41	0	5	3	1	1	3
Rutile	1	3	1	0	0	1	0	0	0	0	0	0
Garnet	18	0	8	63	32	13	23	24	27	19	22	6
Staurolite	14	12	21	4	18	10	9	15	18	18	9	21
Kyanite	12	31	5	7	22	11	23	15	33	29	26	47
Chloritoid	3	0	2	0	1	9	1	2	2	1	1	0
Apatite	2	tr	1	0	0	0	0	0	0	0	0	0
Amphiboles	2	0	0	-	-	-	-	-	-	-	-	-
2) Opaque					Nothing Reported							

(a) Sample (1) corresponds to Kupsch "Athabasca Sands"
Samples (2) to (19) correspond to Mellon Samples (1) to (18)
Samples (20) to (28) correspond to Carrigy Samples (1) to (9)
(b) Location of samples shown in Figure 4
(c) A dash signifies no reference.

Figure 3-5
Map of Sample Locations



(See Table 3–5 for Sample Numbers Shown)

- *(e) The occurrence of some heavy minerals in these samples show in general a consistent pattern. However, wide differences in compositions can also be observed.*

In spite of the fact that the presence of zirconium and titanium minerals in the tar sands have been known for over 20 years, it is not possible to calculate from the literature data the amount of zircon ($ZrSiO_3$) present in any one of the samples discussed. Rutile (TiO_2) is indicated to be present in very small amounts. Further the presence of ilmenite ($FeTiO_3$) was recorded by Clark, see Table 3-4, but no quantities were given. Other workers did not mention ilmenite to be present.

The literature data can be utilized in that the frequency of zircon occurrence in the data can be plotted against the recorded percentage of non-opaque heavy minerals, see Figure 3-6. The average zircon percentage in the non-opaque minerals is estimated there from to be 10.8%. This becomes 7.8% when ignoring the unusually high values of some samples possibly due to small local pockets of zircon laid down by tides in the original formation of the tar sands.

3-3-2 Occurrence

Many deviations from the mineral suite found by others have been noted. Particularly a much better definition of the opaque mineral suite has been obtained. There was little or no reference to the regular occurrence of sulphide, carbonates, and manganese minerals, etc. Quite clearly the occurrence of these minerals should be proven by other tests and further work on many more samples from different locations.

Total heavy mineral content of >2.89 g/ml of solids were obtained using heavy solvent separation techniques. The amount of heavy minerals in the Escarpment and in the Beaver Creek tar sands were determined. The total percentage of heavy minerals, separated from samples of these two differently located tar sands, are shown in Table 3-6. It will be noted that the majority of the Mildred Lake tar sand samples contained approximately 0.7 wt% on total solids or 0.6 wt% on tar sands of heavy minerals. The heavy mineral content of the Beaver Creek plant feed was lower than the Mildred Lake samples.

The amount of mineral fractions excluding sand and clay, i.e. >2.7 g/m, minerals are shown in Table with elemental distributions, as determined by emission spectrographic analyses on the Beaver Creek plant feed solids. It should be noted that particularly the 2.7-2.8 g/ml fraction and the 2.8-2.963 g/ml fraction contained appreciable amounts of very small red and white amorphous like grains together with larger "plate" minerals which are probably hematite, leucoxene and mica, respectively. The total 2.7 g/ml and heavier minerals amounted to less than 1% of the total solids, of which about a third is heavy minerals, >2.963 g/ml. The total heavy minerals appear to be divided into about 30% non-opaque, mainly silicates, and 70% opaques.

(a) Size

The distribution of heavy minerals in different size fractions of Beaver Creek samples are compared with those of Area B in Figure 3-7. Zircon was found to be quite uniform in size in all samples, and to occur almost completely in the 100-325 U.S. mesh size fraction. This is illustrated by the emission spectrograph analyses of Beaver Creek samples in Table 3-7. In general heavy minerals occur as particles greater than 325 U.S. mesh. The larger particles are generally either sulphides, limestone or aggregates of silica cemented together by various heavy minerals.

(b) Non-Opaques

The non-opaques (transparent or translucent), therefore, comprise about 30 wt% of the total heavy minerals, and are mainly silicates, Table 3-8. The non-opaques are very similar to those found in the literature except that the percentages in the Mildred Lake samples deviate somewhat, compared with Table 3-5. The notable exceptions are that zircon was present in a higher average percentage in the Beaver Creek non-opaques and epidote was also more predominant in this particular sample. Tourmaline occurred in about an average of half of the total amount of non-opaques present. All other silicates, such as staurolite, kyanite, garnet, etc, occur in only small percentages. However, the relative amounts of these individual minerals varied in the samples selected for study not only from the same source but between samples from different areas. There are many other significant divergences between the different samples from the

Figure 3-6

Frequency Distribution of Weight Percentages

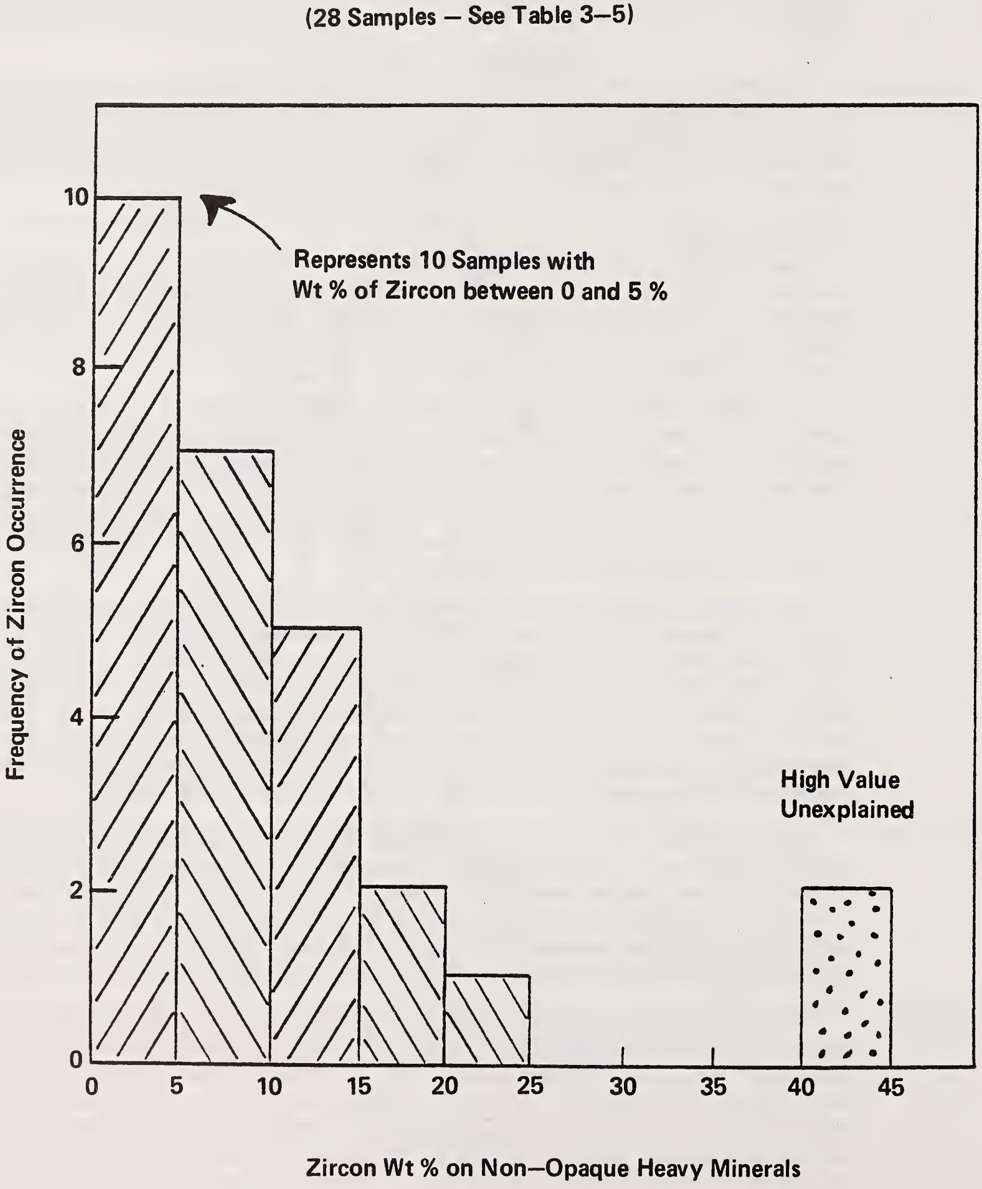


Figure 3-7

Size Distribution of Solids and Heavy Minerals

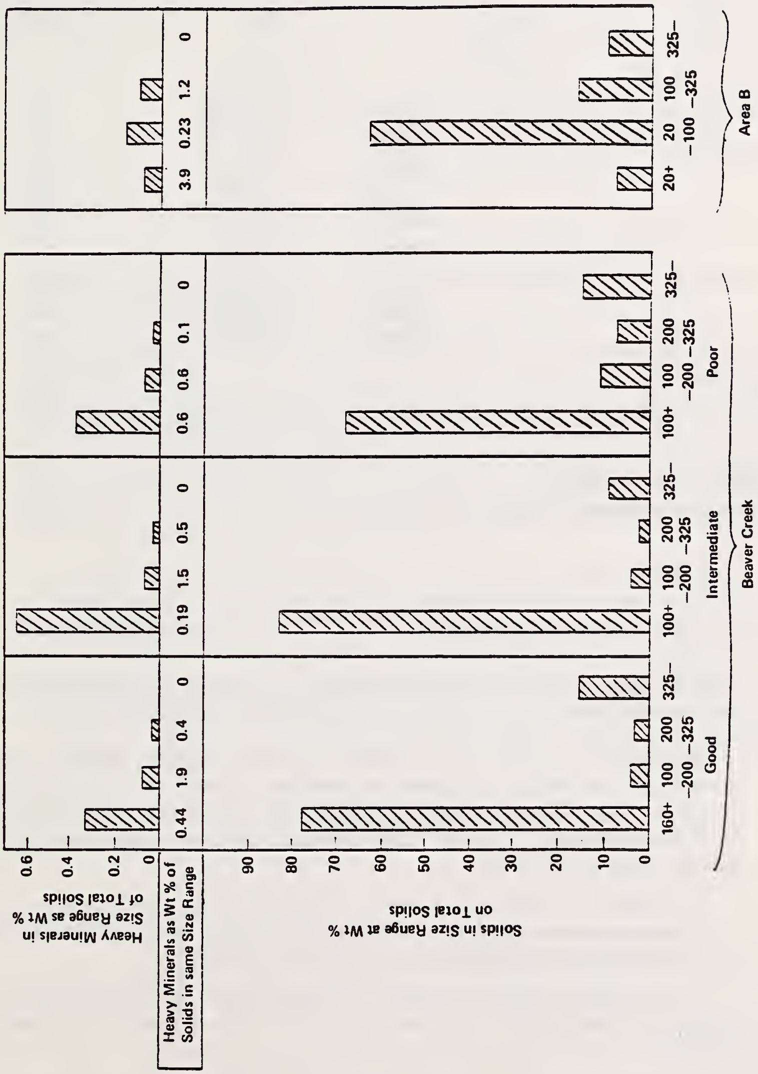


Table 3-6

Heavy Mineral Content of Tar Sand Samples

Tar Sand	Depth	Footage	Total Heavy Mineral* Wt % on Solids
Escarpment Area			
Area B	-	-	0.5
Hole 11	-	-	1.0
Hole 21A	-	-	0.6
Cores			
15-16-2	Top	67-99	0.5
	Middle	115-163	0.5
	Bottom	163-214	0.4
29-16-2	Top	32-63	0.8
	Middle	63-110	0.4
	Bottom	110-174	0.4
34-14-2	Top	79-110	0.5
	Middle	110-159	0.6
	Bottom	174-206	0.3
Good			0.6
Intermediate			0.9
Poor			0.7
Plant feed solids - CSAI extracted			0.31
Plant feed tar sands (received at Sarnia)			0.35

* >2.963 g/ml

Mildred Lake Area. For example, more larger grain garnet were found in samples from the bottom of the formation, e.g. Area B. This agrees with the findings of Carrigy.

(c) Opaques

The oxides that occur are mainly those of iron and titanium, Table 3-9. Oxides of iron that predominate are hematite, magnetite, and limonite. Titanium occurs in a complex oxide with iron in the form of black ilmenite. Only a few grains of rutile (a non-opaque) have been observed in all samples studied. However, a large amount of the titanium occurs as leucoxene, which is a weathered product of ilmenite.

The titanium oxides make up about 25% of the total heavy minerals and are leucoxene and ilmenite in an approximate ratio of 2:1. Iron oxides are the next most abundant heavy mineral in the tar sands and comprised about 16% of the sample counted.

The extent of sulphide occurrence was about 10%. The remaining 20% of the opaques present were made up of a variety of minerals, to which no positive identification has yet been assigned.

Carbonates occur only in very small quantities in the heavy metal fraction. This is because their gravities range from 2.7 (calcite) up to about 3.8 (siderite). It should be noted that siderite, 3.7-3.9 g/ml, should separate with heavy minerals, if not associated quartz, as there is an overlap with the gravity of light minerals. The occurrence of carbonates in heavy mineral fractions are

Table 3-7

Amount and Emission Spectrographs on Denser Mineral fractions

(Beaver Creek Plant Feed Solids)

Gravity Range, g/ml	2.7 - 2.8	2.8 - 2.963	2.963+
Wt % on Total Solids	0.40	0.29	0.31
Major >10%	Si,Fe	Si,Fe	Si,Fe,Ti
Large Minor 5-10%	Al	-	Zn
Small Minor 1-5%	Mg,Ti	Mg,Al,Mn	Mn,Mg,Al,Zr
Large Trace 0.5-1%	Mn,Ca	B,Ti,Zr	B
Small Trace <0.5%	Ba,B,Pb,Me,V,Cu Na,Zr,Ni,Co,Ag K,Cr	Ba,P,Li,Pb,Mo,V Cu,Zn,Na,Ni,Co,Ag K,Ca,Cr	Ba,Pb,V,Cu,Ni,Cr Sr,Ce,Th,Ca Zr,Mo,Co,K

mentioned here briefly, as their role in determining pH and effect on hot water flotation will be discussed in greater detail later.

(d) Distribution

The high gravity solvent separation technique was used to fractionate heavy minerals into rough concentrates. Gravity fractionations of minerals at 3.3 with methylene iodide have successfully concentrated zircon in the heavier fractions. It should be noted, however, that appreciable quantities of titanium occur in the 2.9-3.3 fraction. This is due to the presence of leucoxene in the lighter fractions. The technique of solvent fractionation was investigated as a tool to isolate reasonably large quantities of individual minerals for surface property measurements. However, it appeared to be only suitable as a preliminary concentration step. Other techniques would be required to obtain pure mineral fractions.

The heavy mineral suite separated from the Beaver Creek Plant feed tar sands was fractionated into thirteen fractions using combinations of heavy solvents. Each gravity cut was bout 0.1 g/ml. Accumulative weight percent of the total heavy minerals has been plotted in the summary Figure 3-8 together with individual percentages of the fractions. Very generally, the amount of heavy minerals increased linearly with gravity over the range of 3.0 up to 4.3+ g/ml. The 13 fractions were viewed under a microscope in reflected, transmitted and polarized light to observe the opaques, non-opaques, and birefringence, respectively. The heavy minerals were identified by their crystal shape, colour, and luster. The type of lucite mounts used were not the best, and particle counts made are considered to be preliminary estimates.

The heavy minerals appeared to be composed of three groups.

- *(i) A lighter fractions, sample No. 1-5, which contained appreciable quantities of tourmaline. The grains were average in size and fairly well-formed.*
- *(ii) An intermediate fraction, sample No. 7-9, appeared also to occur. Particularly sample No. 7 was predominantly opaque, small-grained to dust and therefore difficult to judge, and showed alte9ration products and mineral fractions e.g. leucoxene, siderite, amphiboles, pyroxenes and biotite etc. Ilmenite was present only in trace amounts. Samples No. 8 and 9 showed the presence of hematite, leucoxene, staurolite as majors, with some ilmenite pyrites, epidote, kyanite and garnet in smaller qualities. These latter two fractions appeared to contain more well-formed grains.*
- *(iii) A heavier fraction, samples No. 11-13, in which the predominating minerals in these fractions were zircon, leucoxene and ilmenite. Zircon is particularly concentrated in the heaviest fraction (#13) contaminated mainly with brown and black*

Table 3-8

Non-opaque Heavy Minerals

(i) Tourmaline $M^{*}Al_6(OH)_4(BO_3)_3Si_6O_{13}$

Tourmaline occurs in two main forms. First, as larger angular triangular fragments showing evidence of conchoidal curved shell like fracture, and to a lesser extent as well-rounded grains. All particles have a vitreous luster and are transparent. The colour varies with the size of the particle. Small particles appear dark yellow, larger particles are dark brown and green, while larger angular fragments appear black due to the thickness of the cross section. This variety shows frequent yellow-green zonal distribution of colour in a grain. The second form is pink in colour and occurs as long prismatic crystals. This form is thought to be an alkali variety of tourmaline.

(ii) Zircon ($ZrSiO_4$)

Zircon is normally regarded as a mixed oxide of zirconium with silicon. Impurities are often present in the zircon, and these are mainly rare elements such as hafnium, uranium, thorium, rare earths, and sometimes iron. The presence of impurities imparts a fluorescence to the zircon minerals when radiated with short wave UV light. Zircon exhibits a very distinct yellow fluorescence indicating the presence of other metal impurities. The expected impurities also appear in the emission spectrographic analyses. It is interesting to note that zircon obtained from Australia exhibits very little or no fluorescence, whereas zircon from Florida exhibits appreciable fluorescence like the zircon in the oil sands.

The technique of UV fluorescence has been used extensively to ascertain whether zircon has been separated or is concentrated in density fractionation. It has been specifically used to determine whether zircon was present in fractions of lower density, and hence a measure of the degree of separation. It is at present only a qualitative tool, but is indeed very useful in obtaining some measure of the degree of occurrence of zircon. The heavy minerals in general do not appear to exhibit any other type of fluorescence other than that of zircon. A very few green and blue fluorescent crystals have been observed but these are extremely rare.

Emission spectrographs of zircon concentrates have shown hafnium to be also present in what appears to be a fairly constant ratio. Standards were not present for hafnium, comparison of spectrographic line densities at the same intensity enabled a tentative estimate of about 5% hafnium on zirconium to be made. The presence of hafnium is of importance to considerations of economic extraction of zircon for the metallic zirconium with hafnium as an additional product.

Zircon occurs as partially or completely rounded particles. The particle size is uniformly small, in fact that zircon grains are the smallest of the heavy minerals. Grains which retain some crystalline form, tend to be elongated with prismatic habit at either end.

Many of the zircon grains (estimated at ~10% in samples inspected) appear to have absorbed material on their surface which imparts an appearance of being coloured. Frequently this colour is amber to red and on washing with hot HCl some of the zircon achieves its normal splendent luster. This film is believed to play an important role in the flotation of zircon. Quite the bulk of the zircon occurs in well developed crystals with a tetragonal structure, and is colourless and exhibits a vitreous luster. It is very hard and exhibits a high specific gravity.

(iii) Epidote ($Ca_2(Al,Fe)_3O(OH)SiO_4Si_2O_7$)

Epidote occurs as somewhat elongated prismatic crystals. It is blackish green in colour and has a vitreous luster. Due to the thickness and colour of the crystals, transmittance of light is poor.

(iv) Staurolite ($Fe(OH)_2\ 2Al_2OSiO_4$)

This mineral occurs as well developed prismatic crystals as well as rounded grains. It is yellow with a slight amber tinge, and has a vitreous luster, although it commonly appears dull. The crystals are frequently twinned mainly in knee-shape forms.

(v) Garnet (M_3 "M_2"' ($SiO_4)_3$)**

This mineral occurs more frequently in the larger size range, particularly from tar sand samples obtained from the bottom of the formation. The particles are angular fragments showing evidence of conchoidal fracture. The grains are transparent, and the colour is a clear light pink. Emission spectrographic analyses of a few isolated grains showed Mg and Al to be main components, together with some Fe, Cu, and Ca. This suggests the main form of this mineral is $Mg_3Al_2(SiO_4)_3$ or pyrope, which is consistent with its rose coloured appearance.

(vi) Kyanite (Al_2OSiO_4)

Kyanite occurs as transparent perfectly clear crystals. These crystals tend to be flake-like, and show evidence of cleavage planes perpendicular to the length of the crystal.

* Where M represents various amounts of Na, Li, K, Fe, Mg, Mn, Ca.

** Where M" may be Ca, Mg, Mn or ferrous ions and M"' may be Al, Cr, or ferric ions.

Table 3-9

Opaque Heavy Mineral Oxides

(i) Hematite (Fe_2O_3)

Hematite comprises about 1/3 of the iron oxides present in the heavy minerals. It is generally present as opaque reddish-brown masses, which appear to be somewhat amorphous in character. Distinct crystals have not been observed. Frequently it occurs in the form of thin scales, which are very red in colour.

(ii) Magnetite (Fe_3O_4)

Magnetite occurs to an appreciable extent in the heavy minerals, and comprises about 1/3 of the iron oxides present. It exhibits very strong magnetic properties, and was separated in an isodynamic separator by adherence to the upper magnet. It occurs as mainly small well-formed black opaque crystals, which frequently show octrahedral face with rounded edges. Another magnetic form occurs in the tar sand minerals as larger somewhat amorphous masses with a submetallic to dull luster compared with the splendent luster of the smaller magnetic crystals. This mineral occurs in about a 1:1 ratio with the black magnetic crystals in the most magnetic material separated from the heavy minerals suite in isodynamic separation. The larger amorphous material could be either magnetite or a type of specular iron (hematite). The latter is observed to occur occasionally interbedded with reddish-brown almost granular hematite in a mass. However the hematite could also occur as an alteration product of the magnetic magnetite. This is not important as both these materials may be regarded as effectively inert in the hot water process.

(iii) Limonite ($HFeO_2$)

Limonite occurs in amorphous and porous masses, which were yellow (ocher) to yellowish-brown in colour. It frequently occurs with silica particles in aggregates. The shape of the limonite masses often parallels that of pyrites (FeS_2) in being spherical or dumbell-like and also in its association with quartz. It is believed that limonite occurs through oxidation of pyrites. Hydrogen peroxide studies resulted in the conversion of pyrites to limonite. This oxidation reaction effectively accelerates the natural process. It is believed that the presence and amount of limonite in a sample may be a measure of the degree of oxidation that has taken place.

(iv) Ilmenite (Variable mixed oxide $FeOTiO_2$)

Ilmenite occurs as well-rounded or as angular particles. The size varies widely. Some grains were as small as zircon, while others are as large as the larger heavy mineral grains excluding aggregates and sulphides. The grains are black and opaque with a submetallic luster. In certain light, the surface glints as if from submicroscopic crystalline formation on the surface. The streak colour (i.e. the colour obtained by scratching the surface of a rock) may be observed with microscopic mineral grains by crushing them. The powder obtained by crushing ilmenite grains was brownish-black.

(v) Leucoxene (a TiO_2 form)

Leucoxene occurs in appreciable quantities. Leucoxene is a very ill-defined oxide of titanium, which is snow-white in appearance and results from the weathering or natural leaching of iron from ilmenite. It is quite variable in gravity as it occurs in all density samples to an appreciable extent. In some of the middle gravity fractions of the heavy minerals, grains of ilmenite can be seen to have weathered to leucoxene on the crystal perimeter. Likewise some grains of leucoxene have been observed with ilmenite incrustacions. In general, the ratio of ilmenite to leucoxene in the tar sands is estimated to be about 1:2. Titanium was found throughout the gravity range of the heavy minerals, even in the 2.7 - 2.8 g/ml fractions - see Table 17, and of course reflects the presence of leucoxene observed throughout all lighter mineral fractions.

Leucoxene, although occurring mainly as the white variety, has been observed as a yellow - white form probably with iron contamination, and as a pinkish form indicating manganese contamination. This is not unexpected as manganese can occur in ilmenite.

---

* A magnetic separator with variable field, which separates a stream of magnetic grains from a sample of particles flowing down an incline under vibration.

grains, which appear to be mainly ilmenite and magnetite. Hematite was also present with small amounts of pyrites and some epidote. There were other crystals unidentified in this fraction. It should be noted here that if uranium occurs in the form of the mineral uranite, it would tend to occur in this fraction as either a brown or a black dull mineral. Its' identification therefore is difficult in sample No. 13 with other dark opaque minerals present.

The general description obtained of the fractions of heavy minerals gave a rough picture of the occurrence of different types, relative to their density and degree of separation. This was shown pictorially in the summary Figure 3-8. The values are only of approximately the right order of magnetitude. The diagram illustrates that fractionation achieves only rough concentration of major minerals. There appears to be so much overlap in gravity that this is not too good a method for obtaining pure mineral fractions for further study. However these fractions may prove more suitable for X-ray analysis than the total heavy mineral suite, which is too complex for good resolution.

The recovery of zircon, for zirconium, may be attractive, particularly with the estimated hafnium content of 5% as a byproduct. However, the total titanium in the tar sands does not reflect the availability of titanium for ready recovery as ilmenite (low rutile).Its' occurrence as leucoxene presents a complicating factor, reducing recovery of titanium to perhaps only a third of the total titanium. The lower amount of total heavy minerals found in the Beaver Creek Plant Feed solids, however, will decrease the incentive for economic extraction of desirable minerals as byproduct to oil recovery, if this is a representative sample of the area. Owing to the physical state of the minerals, separation of individual members may prove to be quite difficult, and extensive studies would have to be undertaken to obtain data, if economics suggest potential for byproduct minerals.

(e) Magnetic Minerals

After gravity separation of the heavy minerals from the Beaver Creek sample, an attempt was made to separate the heavy minerals on the basis of their magnetic properties. This was tried in a Franz isodynamic separator. This technique is time consuming, and as this work was attempted in London*, only a few separation passes were obtained at high magnetic field strengths. Very little difference in mineral distribution was observed between streams collected from the separator. The main difficulty in effecting separation was due to the wide variety of grain sizes in the sample.

Some of the heavy minerals adhered to the upper magnet, hence showing very strong magnetic properties. This material was collected and it was found to be mainly oxides of iron, e.g. magnetite with some hematite. This may be useful in further identification studies of heavy fractions, >4.3 g/ml, as well as a step for purifying zircon concentrates by magnetite removal.

In summarizing the occurrence, the mineral types and amounts vary appreciably with location and depth in the deposit. As it is a sedimentary deposit, local concentrations of heavy minerals occur, which are almost non-existent in other locations, e.g. sphalerite. Differences are indicated by comparison of emission spectrograph analyses. A typical elemental analysis of heavy minerals is given in the following table:

TYPICAL ELEMENT AL ANALYSIS OF HEAVY MINERALS

Majors	10%	Si, Fe, Ti
Minors	1-10%	Mg, Mn, Al, Zr, S
Traces	1%	B, Ca, cu, Ba, K, Co Ni, P, Sn, V, Li, Pb
(Possible Trace elements)		Hf, U, Th, Sc, Ce, Y, Lu

*University of Western Ontario

The elements present are generally consistent with the minerals identified.

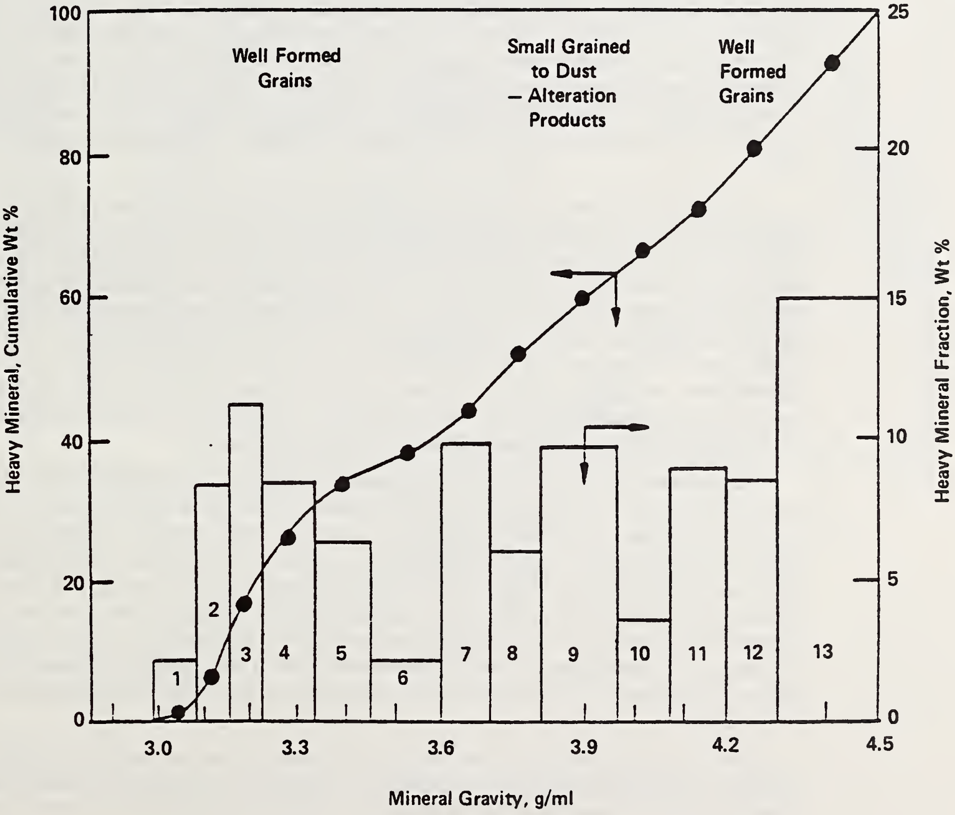
Gravity fractionation of heavy minerals was carried out using heavy solvent techniques. Quantities of fractions are shown in Figure 3-8. The compositions of the various fractions are shown pictorily in Figure 3-9. The main point of this plot is to point out that about two thirds of

Figure 3-8

Mineral Gravity Distibution in Total Heavy Minerals Extracted from Beaver Creek Tar Sands

Sample Number	Gravity Range	wt % on total	Sample Number	Gravity Range	wt % on total
1	2.98-3.08	2.2	8	3.70-3.80	6.0
2	3.08-3.15	8.3	9	3.80-3.96	9.7
3	3.15-3.22	11.2	10	3.96-4.07	3.5
4	3.22-3.33	8.4	11	4.07-4.19	8.9
5	3.33-3.45	6.5	12	4.19-4.30	8.5
6	3.45-3.59	2.1	13	430+	14.9
7	3.59-3.70	9.8			

* 0.3 wt % on Total Solids



the titanium present is in the form of leucoxene, a white weathered oxide formed from iron leaching of ilmenite. It has a variable gravity like pyrites, although in this latter case it is due to quartz (2.65 g/ml) association.

Although there are many similarities with the findings of other workers reported in the literature, many differences in mineral occurrence have been observed. Particularly, a much better definition of the opaque minerals has been obtained. There was little or no reference to the regular occurrence of sulphides, carbonates, and the occurrence of manganese had not been mentioned previously.

The occurrence of minerals containing these chemical groups should be proven by other tests, and further work should be carried out to define particularly sulphides and their impurities and the total occurrence of carbonates with types and amounts.

3-3-3 Elements

Emission spectrographic analyses have been carried out on heavy minerals separated from the several characterization samples of Mildred Lake and Beaver River tar sands. The results are presented in Table 3-10 and 3-11.

It will be observed that the major components in all the tar sands are silica, iron and titanium. Magnesium, manganese, aluminum, and zircon occur in up to 5% in most samples. As a large trace, boron indicated the presence of tourmaline in appreciable quantities in all samples. The small amounts of different metals are in general similar, however, a few points may be noted, particularly from comparisons of emission spectrographic lines from different samples. Calcium appears to occur in larger quantities in tar sands samples from the bottom of the formation than in samples taken from the top of the formation. It is not yet clear that this parallels an increase in calcite with increasing depth in the formation, and is related to processability. For example 29-16-2 tar sands, which exhibited good processibility, also contained large traces of calcium.

Another point is that zinc occurs in a higher quantity in 29-16-2 than in all other tar sand solids inspected. This element appears to vary widely even between samples. Uranium in trace quantities also appears to vary quite significantly from sample to sample and does not appear to parallel zircon occurrence, which suggests it is not necessarily an impurity of this mineral. The emission spectrographic lines of uranium are quite intense with samples that are taken from the top of the formation, whereas tar sands from the bottom of the formation exhibit only weak intensity lines. The presence of uranium could be of great importance if it occurs as a distinct mineral, such as uranite. Yttrium, thorium, cerium, and lutecium have been observed to be present in trace amounts with lead, but standards have only recently become available for determining the possibility and extent that these rare metal might occur.

The elements of the heavy minerals separated from Bench Unit froths from 29-16-2 bottom and Hole 11 tar sands as well as those from four Beaver Creek tar sands are shown in Table 3-11. It will be noted that in general the elements are similar to those recorded in Table 3-10, but that significant differences do occur. For example in Beaver Creek good tar sands, potassium and lithium are present in larger amounts and titanium in slightly less amounts than in other samples. Although it is not known whether intermediate and bad tar sands are taken from the top of the Beaver Creek formation, it is interesting to note that the uranium lines in these samples were very intense, indicating significantly larger amounts in both these samples compared with standard lines. However, it was not possible to determine radioactivity above background noise with a gauge counter.

Heavy minerals in different size fractions of Beaver Creek tar sands, top of Table 3-12, generally confirmed microscopic observations of minerals. For examples, tourmaline occurs as selectively larger minerals form and ziron occurs as well formed but micelles mineral forms.

The 13 fractions and the total heavy minerals were submitted for semiquantitative emission spectrographic analysis. The samples were run against 4 standards and at three levels of concentration. By interpolating line densities the percentage of elements present were estimated. From the analysis it appeared that the metal content was over 50 wt%. Unfortunately the majors

Figure 3-9

A General Description of Minerals from Gravity Fractionation of Beaver Creek Tar Sands

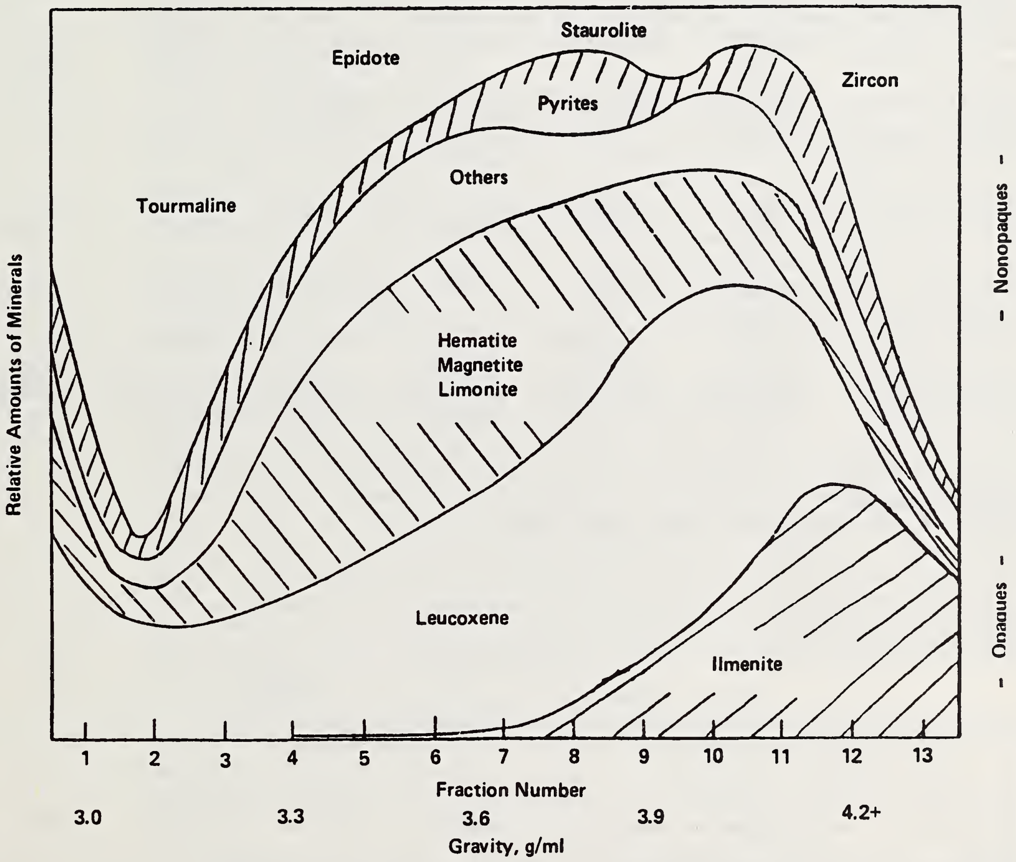


Table 3-10

Emission Spectrograph Analyses of Heavy Minerals

from Characterization Study

Tar Sand Source	Area B	Hole 11	Hole 21A	15-16-2		
				Top	Middle	Bottom
Major >10%	Si,Fe,Ti	Si,Fe,Ti	Si,Fe,Ti	Si,Fe,Ti	Si,Fe,Ti	Si,Fe,Ti
Large Minor 5-10%	-	-	-	-	-	-
Small Minor 1-5%	Mg,Mn,Al,Zr	Mg,Mn,Al,Zr	Mg,Mn,Al,Zr	Mg,Mn,Al,Zr	Mg,Mn,Al,Zr	Mg,Mn,Al,Zr
Large Trace 0.5-1%	B,Ca	B	B	B	B,Ca	B,Ca
Small Trace <.5%	Zn,Cu,Ni,P	Zn,Cu,Ni,Ca,P	Zn,Cu,Ni,Ca,P	Zn,Cu,Ni,Ca,P	Zn,Cu,Ni,P	Zn,Cu,Ni,P
Ba,Hf,V,U	Ba,Hf,V,U	Ba,Hf,V,U	Ba,Hf,V,Th,U	Ba,Hf,V,U	Hf,V,U	
Wt % on total solids	0.5	1.0	0.6	0.5	0.5	0.4

Tar Sand Source	29-16-2			33-14-2		
	Top	Middle	Bottom	Top	Middle	Bottom
Major >10%	Si,Fe,Ti	Si,Fe,Ti	Si,Fe,Ti	Si,Fe,Ti	Si,Fe,Ti	Si,Fe,Ti
Large Minor 5-10%	Mg,Al	-	-	-	-	-
Small Minor 1-5%	Mn,Zr	Mg,Mn,Al,Zr	Mg,Mn,Al,Zr	Mg,Mn,Al,Zr	Mg,Mn,Al,Zr	Mg,Mn,Al,Zr
Large Trace 0.5-1%	B,Zn,Ca	B,Zn,Ca	B,Ca,Zn	B,Ni	B	B,Ca
Small Trace <.5%	Cu,Ni,K,P	Cu,Ni,K,P,Hf	Cu,Ni,K,P	Zn,Cu,Ca,P	Zn,Cu,Ca,Ni,V	Zn,Cu,K,Ni
	V,Hf,U	V,Pb,U,CO	V,Pb,U,Hf	Sn,V,Hf	(Sc and Ce trace)	Hf,U
Wt % on total solids	0.8	0.4	0.2	0.5	0.6	0.3

Mg, Mn, Al are close to 5%.
Hf, U, V, Lu, Th, Ce are known to be present in small amounts but no standard.

Table 3-11

Emission Spectrograph Analysis of Heavy Minerals

Tar Sand Source Bottom	29-16-2	Hole 11	Plant Feed	Good	Intermediate	Bad
Starting Material	Bench Unit Froth		Tar Sands			
Major >10%	Si,Fe,Ti	Si,Fe,Ti	Si,Fe,Ti	Si,Fe,Ti	Si,Fe	Si,Fe
Large Minor 5-10%	-	-	-	Mn	-	-
Small Minor 1-5%	Mg,Al,Mn,Zr	Mg,Al,Mn,Zr	Mg,Al,Mn,Zr	Mg,Al	Mg,Zr,Mn	Mg,Al,Zr,Mn
Large Trace 0.5-1%	B,Zn	B	B,K	B,Zr,K,Ca,Zn	Al,Ti,Ni,K,U	B,Ti,Ni,K,U
Small Trace <.5%	Ca,V,Cu,Ni,K Pb,Hf	V,Cu,Ni,Ca Ba,P,Hf,Zn	Ba,Pb,Mo,V,Cu,Hf Na,Ni,Ca,Cr,Co	Ba,Sb,Li,Pb,Sn Mo,V,Cu,Na,Ni Co,Ag,Cr,U	Ba,B,P,Li,Sn Pb,Mo,V,Cu,Co Ag,Ca,Cr,Hf	Ba,P,Li,Sn,Pb Mo,V,Cu,Co,Ag Ca,Cr,Hf
Wt % on total solids	0.2	1.0	0.3	0.6	0.9	0.7

were estimated as greater than 10%.The high metal percentage, however, is quite consistent with the occurrence of mainly oxides, silicates, and sulphides, which has been discussed before. The detailed analysis is shown in Table 3-13. The major elements are shown at the top of the table, and the minor elements comprising about 8 wt% of the total heavy minerals, are shown at the bottom of the table. This is a first attempt, and more standards will be used to achieve greater precision with future samples.

(a) Majors

Silica reflects the silicate minerals present, as well as a very small amount of quartz which are attached primarily to the sulphides present. Iron is present mainly as the oxides discussed before. Titanium occurred in the form of mostly leucoxene with some ilmenite and less rutile. Leucoxene has a very variable gravity and is therefore reflected in all the different density fractions. The technique of fractionating these heavy minerals was particularly satisfactory for concentrating the heavier minerals, e.g. zircon, as evidenced by a high percentage in samples #11, #12 and especially #13, Figure 3-8.

It was most surprising that zinc was found in such a high concentration of 8% in this particular sample (although there may be interference from unknowns).Other Beaver Creek plant feed samples showed considerably less zinc to be present, Table 3-11. White-grey, micro-crystalline, metallic masses suggest the presence of zinc in the form of mainly sphalerite. The presence of zinc in this large amount was unexpected not only in view of the results obtained with previous samples shown in Tables 3-13, but also as mentioned in the literature. The twelve Mildred Lake characterization samples, Tables 3-10, showed in general the same similar suite to that of the Beaver Creek plant feed, Table 3-11, but with lower quantities of zinc i.e. <1.0% . The significant difference of higher zinc in the case of the Beaver Creek plant feed solids sample used would indicate that certain minerals do occur more as a function of an immediate local zone.

(b) Minors

It is surprising that uranium lines were observed in practically all our samples. The lines however were faint in the earlier samples, which presumably was due to the fact that the solid samples were mainly from the bottom of the deposit. Recent samples however appear to contain appreciable more uranium as compared to the standard emission spectrographic line. It will be reiterated at this point, that the lines may occur as interference lines from unknowns present. Inspection of the data in Table 3-13 will show that the uranium increases appreciably in the heavier fractions. This parallels both the occurrence of zircon as well as gravity of possible uranium minerals, such as uranite or pitch blend. Quite clearly the presence of uranium should be more fully investigated. The evidence in favour of uranium being present to date is that it appears in the emission spectrograph analysis compared with standard. The further detection against standards of thorium, cerium and lead that are all elements that occur with uranite; could be substantiating evidence.

It should be noted that manganese occurred in about 1% of the Beaver Creek heavy mineral surface. This appeared to be lower than values from other samples, Tables 3-10 and 3-11, in which the emission spectrographic lines indicated closer to 5% for manganese. Hence, a brief study was undertaken to try to find in what form the manganese occurred. The observations made are recorded separately, in Table 3-14, but are by no means conclusive.

In summary, the occurrence of manganese in the heavy minerals is unusual and unexpected. However, this may be explained in terms of the alkaline pH of the tar sands. Its high solubility in "aged or acid" tar sands is similar to its behaviour in soil chemistry. As it can be tied up in the insoluble hydroxide form by adjusting pH, its behaviour will be similar to that of ferrous rather than calcium or magnesium. However, its chemistry should be more fully developed, and its relationship to hot water flotation process explored further.

(c) Analysis

It should be pointed out that the most striking aspect of this emission spectrograph work was the appearance of many intense lines in the samples which were absent in the standards comprising about half of the common metals in the periodic table. The appearance of many lines from unknown elements present in at least trace amounts can cause considerable uncertainty in the prediction of even well known elements. This uncertainty applies even more so to the uranium line, which although being intense, occurs in a region where there are several intense lines not

Table 3-12

Miscellaneous Emission Spectrographs Analyses of Heavy Mineral Fractions

Heavy Minerals	**Beaver Creek Tar Sand**		
	(100+ Mesh)	**(100-200 Mesh)**	**(200-300 Mesh)**
Major <10%	Fe,Ti,B,Si	Ti,B,Si	Fe,Ti,Si
Large Minor 5-10%	-	Fe,Al	-
Small Minor 1-5%	-	Mg,Zr,Lu	Zr,Mg
Large Trace 0.2-1%	Mn,Mg,Al,Cr,Lu,V	Cr,V,Ca	Mg,B,Lu,Al,V,Cr
Small Trace <0.2%	Pb,Cu,Ca	Cu,Hf	Cr,Ca

Heavy Minerals(a)	**Hole 11 Tar Sand**		**29-16-2 Tar Sand**	
	Sp. Gr. 2.9-3.3	**Sp. Gr. 3.3**	**Sp. Gr. 2.9-3.3**	**Sp. Gr. 3.3**
Wt % on Froth Solids (aeration)	1.2	6.7	1.1	2.6
Major <10%	B,Si,Fe	Si,Fe,Ti	Ti,B,Si,Fe	Si,Fe,Ti
Large Minor 5-10%	-	-	-	Zr
Small Minor 1-5%	Ti	Zr	-	B,Lu,Mg,Ni
Large Trace 0.2-1%	Lu,Na	B,Lu,Ni	Mg,Lu	Pb,Al,Hf,Cu
Small Trace <0.2%	Mg,Pb,Al,Ca,V Cu,Ni	Mg,Hf,Pb,Al Ca,V,Cu,Cr	Pb,Al,Ni Cu,V,Ca	V,Ca,Cr

	Froth Solids			
Heavy Minerals(c) From:	**Hole 11B "TOLCO" Solids (Rapid Settling in Bromoform)**	**Slow Settling Fines(b)**	**C.S.A.I. #589**	**C.S.A.I. #590**
Wt % on Total Solid Fraction	35.8	23.0	7.8	10.4
Major <10%	Ti,Fe,B,Si	Ti,Fe,Si	Fe,Si,Ti	Fe,Ti,Si
Large Minor 5-10%	Zr	B	-	-
Small Minor 1-5%	Mg,Al,Mn	Mg,Al,Mn	Mg,Zr,Mn	Mg,Al,Zr,Mn
Large Trace 0.2-1%	V,Ni,Ca	V,Ni,Ca	B,Al,Zn,Ni,Co,U	B,Zn,Ni,Co,U
Small Trace <0.2%	Cu,Ca	Cu,Zr,Cr	Ba,P,Li,Sn,Pb,Mo V,Cu,Ag,K,Ca,Cr	Ba,P,Li,Sn,Pb Mo,V,Cu,Ag,K Ca,Cr

(a) Fractionation of heavy minerals with methyl iodide (sp. gr. 3.33)
(b) A second lot of heavy minerals obtained by settling overnight
(c) Samples of "TOLCO" solids and CSAI #589 and #590 received from Edmonton

Table 3-13

Emission Spectrograph Analyses of Heavy Minerals (>2.96g/ml) from Beaver Creek Plant Feed

Gravity Fraction(2)	Total	1	2	3	4	5	6	7	8	9	10	11	12	13
Major Elements														
Silica (Si)	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	5.0	5.0	10.0
Iron (Fe)	10.0	10.0	5.0	7.0	7.0	10.0	10.0	10.0	10.0	5.0	10.0	5.0	5.0	5.0
Titanium (Ti)	10.0	10.0	4.0	4.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Zinc (Zn)(3)	(8.0)	0.001	5.0	5.0	5.0	8.0	9.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Zirconium (Zr)(1)	4.0	0.08	0.08	0.08	1.0	1.0	1.0	1.0	1.0	1.0	1.0	5.0	5.0	10.0
Minor Elements														
Sodium (Na)	0.1	0.1	0.4	0.1	0.01	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Potassium (K)	0.01	0.06	0.1	0.03	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Magnesium (Mg)	1.0+	5.0	1.0	1.0	1.0	0.4	0.5	0.1	0.1	0.5	0.5	0.1	0.1	0.1
Calcium (Ca)	0.6	1.0	0.8	0.8	0.8	0.5	0.5	0.5	0.5	0.5	0.5	0.4	0.4	0.5
Barium (Ba)	0.08	0.08	0.05	0.05	0.1	0.1	0.08	0.08	0.08	0.08	0.08	0.08	0.05	0.05
Strontium (Sr)	0.1	0.1	0.1	0.01	0.01	0.07	0.1	0.1	0.1	0.05	0.05	0.1	0.1	0.1
Manganese (Mn)	1.0+	0.5	0.2	0.5	0.5	0.1	0.1	1.0	1.0	0.8	1.0	0.1	0.1	0.1
Aluminum (Al)	1.5	2.0	8.0	5.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Copper (Cu)	0.05	0.08	0.06	0.1	0.01	0.05	0.01	0.01	0.1	0.05	0.005	0.01	0.01	0.08
Nickel (Ni)	0.2	0.08	0.08	0.1	0.1	0.05	0.08	0.08	0.08	1.0	1.0	0.1	0.05	0.1
Cobalt (Co)	0.05	1.0	0.01	0.01	0.01	0.05	0.05	0.1	0.1	0.07	0.07	0.05	0.05	0.1
Chromium (Cr)	0.1	0.08	0.07	0.07	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.3	0.5
Vanadium (V)	0.5	0.07	0.1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Molybdenum (Mo)	0.01	0.07	0.01	0.01	0.01	0.01	0.01	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Boron (B)	0.5	0.5	1.0	1.0	0.08	0.5	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.005
Phosphorus (P)	0.5	0.5	0.5	0.7	1.0	1.0	0.8	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Uranium (U)(3)	(1.0)	(0.1)	(0.1)	(0.1)	(1.0)	(1.0)	(1.0)	(0.8)	(0.7)	(0.1)	(0.1)	(1.0)	(2.0)	(5.0)
Cerium (Ce)	0.1	0.1	0.1	0.1	0.1	0.1	1.0	1.0	1.0	1.0	1.0	0.1	0.1	0.1
Thorium (Th)	0.1	0.1	0.1	-	-	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1

Others Present: Lead (Pb) = 0.05; Tin (Sn) 0.0005 (Mainly in fractions 2-5); Silver (Ag) = 0.01; Columbium = 0.01 (Mainly in fractions 5-9). Yttrium (Y) = 0.01.

(1) Hafnium (Hf) is also present occurring with zirconium. Estimates by comparison of line densities at equivalent intensity shows hafnium to be approximately 10% of zirconium values.

(2) See Figure for gravity ranges.

(3) These high values may reflect interference from unknowns.

present in the standards. It is, therefore, required that many of the elements present in these minerals should be further identified, and that other tests be used to confirm these findings.

3-3-4 Froth Solids

The distribution of heavy minerals in hot water flotation as determined by settling the oil-free solid fractions in bromoform, was found to be 60% in the froth and 40% in the sand for an Area B tar sand. There were no heavy minerals in the water phase solids.

The heavy minerals in the froth represented about 30% of the solids present and contained all the titanium and zirconium. There was no trace of these metals in the heavy minerals separated from the sand phase. As flotation partially separates and hence concentrates the heavy minerals in the froth solids, these solids would be a logical stream for further separation to recover individual minerals, especially zircon, if economically attractive. Hence, definition of the solids in the froth, obtained either by aeration in separation or with only entrained air in mixing, were carried out.

Froth obtained with aeration contain appreciably more total solids. Heavy minerals were not removed to any appreciable extent by water washing, but separated almost completely with solvent dilution and settling, Table 3-15. Essentially all the zircon and ilmenite appeared to be concentrated in the froth and were removed by in froth cleanup solvent dilution and separation. This indicates that the heavy minerals are essentially water-wet, but undergo either flotation in the process due to adsorption of naturally occurring surfactants that cause attachment to air introduced into the system, or follow the bitumen by attachment.

Sodium tripolyphosphate was found to be a most effective additive for separating the bulk of the solids from the froth without dilution with solvent in small scale exploratory studies. It was superior to sodium hydroxide, carbonate, silicates, phosphates and pyrophosphate. Studies with combinations of sodium cripolyphosphate (1% on Froth) and a Breaxit (#941) demulsifier (0.1% on froth) showed that solids removal was achieved through the addition of the sodium tripolyphosphate. The Breaxit was not apparently effective by itself or in combination with the inorganic additive, but mostly reduced the water in the oil phase. Use of a solvent to reduce the viscosity (1:1 solvent to oil ratio), gave a degree of separation at a greatly increased rate. The bulk of the solids were readily removed from this type of froth which tend to be oil-wet. Emulsion problems were almost completely overcome with combinations of sodium tripolyphosphate and solvent.

Froth obtained from separations with only air entrainment in mixing in the C.S.A.I. pilot unit have considerably lower solids contents. These solids are also more difficult to remove since they are more closely associated with the oil. The heavy mineral content of these froths was ~15 to 20 wt% of the solids, for example Table 3-16, compared to ~0.7 wt% for oil sand. The types of heavy minerals present are typical of the general total suite e.g. zircon occurred in about 5-10%. Thus heavy minerals appear to be greatly concentrated in the froth by flotation. This indicates that froth solides may be a good feed for heavy mineral recovery.

A very fine heavy mineral "dust" of E mesh exists in practically all extracts from froth samples. Presumably most of these fines result from minerals with low hardness values. It would normally occur in the 325 mesh fraction with clay minerals, chert (quartz), and "mica dust". Frequently, it is held in suspension in the heavy solvent separation. This fine material has been observed to occur (concentrated) more in solid samples derived from froth.

A particularly good example is given at the bottom of Table 3-12 for "Tolco" solids (froth after roller dewatering). In this example, about 2/3 are well formed heavy minerals that settle rapidly in heavy solvents used for separating from silica. Well formed tourmaline and zircon are typical of this fraction. The remaining fraction of keeping minerals is much slower to settle. Probably best classified as silt, it has also been observed to occur in emulsions (solvent dilution) and as oil-wet solids to an appreciable extent, e.g. froth solids from Bench #1 Beaver Creek Tar Sand extractions. However, by virtue of size, the heavy mineral silt can come into close contact with the oil and hence become tightly associated with the surface of the oil. In this way it passes through the hot water flotation process associated with the bitumen. However as it is essentially water wet it can separate with solvent dilution and centrifuging, but may incur some oil losses.

Table 3-14

Occurrence of Manganese

The analysis of the elements in the heavy minerals, complements and aids the microscopic observations of individual minerals. For example, the occurrence of manganese in the heavy mineral fractions is unexpected based on literature data. The fact that manganese goes readily into solution also suggested manganese is not present entirely as its oxide form pyrolusite (MnO_2).

Fairly large columnar masses, which are deep reddish-brown in colour with deep striations have been observed occassionally. These minerals react with acid with liberation of chlorine and hence are believed to be manganite $MnO(OH)$. The reaction with hydrochloric acid to evolve chlorine is characteristic of this mineral(12). A grey-black dull submetallic mass occurs more frequently in minerals from poor processability tar sands. It is a loose amorphous mass interbedded with quartz crystals and readily can be fractured. It is a very reactive component in the tar sands towards hydrogen peroxide. Separation under the microscope and emission spectrographs have shown barium, manganese, iron and some copper to be present. This could indicate the presence of psilomelane ($BaMnMnO_2$) or perhaps a mixture of pyrolusite (MnO_2) and barite ($BaSO_4$) with iron minerals. Further work is necessary to reveal the nature of this manganese mineral. Several isolated pink crystals have been observed, which from appearance are probably rhodonite ($MnSiO_3$), but these are rare. Rhodocrosite ($MnCO_3$) may occur in purple tinged-yellow masses which exhibit effervescence with acid.

The Mn:Fe ratio of various independent marine sediments is generally of the order of 0.014-0.017. The ratio of Mn:Fe in the tar sands is many times greater than this value which is quite surprising and unexpected. The high Mn:Fe observed in the reduced sediments of the tar sand deposit is similar to that found for deep sea sediments which have about six times the normal ratio as those in the lithosphere.

There are two chemical processes, which determine the amount of manganese in sediments. The first is the leaching of divalent manganese into solution mainly as the bicarbonate. The second is precipitation of various soluble hydroxides. The leaching process is dependent very much on the pH. When the pH is less than 4, leaching of manganese is carried out most efficiently. In the range of pH of 7 to 8, the manganese is strongly fixed as insoluble hydroxides or oxides. This is quite consistent with our observations that manganous is present in solution only in small quantities for normal alkaline tar sands, and the amount in solution increases remarkably with lower pH's. This parallels the well known deficiency of manganese, which causes injury to crops in the different pH soils, since manganese is important in small quantities to life processes.

The manganese in the reduced sediment of the tar sands deposit would be expected to be mainly in the form of manganous, and under non-oxidizing conditions in carbonated water would form the very slightly soluble manganese bicarbonate. The process of selective solutions applies in that manganese is preferentially dissolved over iron, because $Mn(OH)_2$ is a much stronger base than $Fe(OH)_2$. Thus even under the reducing conditions of the tar sands, immobilization of manganese occurs due to the higher pH generally of about 8, determined by the presence of carbonates.

It is interesting that various carbonates of reduced divalent states such as Fe and Mn, or isostructural carbonate mixtures such as manganiferous ankerite $Ca(Fe, Mg, Mn)(CO_3)_2$ could occur in the tar sands. Another form in which manganese might occur is the sulphide. This is isostructurally compatible with calcium sulphide and may occur as the observed green sulphide which is highly reactive to acid conditions. Manganese can also concentrate in an FeS phase in iron sulphides which also occur in the tar sands, as well as to an appreciable extent in many minerals due to atomic size substitution between Mn, Ca, Fe, Ni, and Co.

The possible presence of maganite in alkaline tar sands may therefore not be unusual, and its appearance as a striated form would suggest some leaching probably through bicarbonate dissolution, as evidence by its presence in solution in the water phase of fresh tar sands.

In perspective, this is only a very minor component of the minerals in the oil sands.

3-4 Reactive Minerals

The bulk of the minerals are an inert group with a low solubility, and are not too reactive chemically. However, two important reactive groups of minerals are present. These are sulphides and carbonates.

The occurrence of small masses of quartz cemented together into aggregates to the outside of certain mineral grains has been observed. The cementing material was also found to be the most reactive of all the minerals to acid and oxidation conditions. The four main types of cementing material that appeared to occur most frequently, are

- (1) carbonates that react under dilute acid conditions to give an evolution of carbon dioxide. The carbonates appear to be those containing ferrous, calcium, and magnesium cations (manganous may also occur).
- (2) sulphides, that have been observed to be mainly pyrites (FeS_2), chalcopyrites ($CuFeS_2$), or perhaps sphalerite (ZnS).
- (3) oxides, such as hematite, that are less frequent and more resistant type of cement, that is probably a degraded form of siderite.
- (4) grains of a grayish-black, amorphous material, that appears from emission spectrographic analysis to contain appreciable iron, some barium and manganese, and is very reactive to H_2O_2 leaving a brittle residue.

Observations on these sulphide and carbonates are summarized in Table 3-17.

The association of quartz with iron compounds particularly carbonates and sulphides extends from massive occurrence, i.e. 40 mesh, to also very fine partial films of absorbed material on the surface of the quartz crystals. These films have frequently been observed to be incomplete on any one particular grain and the number of grains having films varied with the tar sand samples. These films can be removed by acid treating. The resulting solution gave a positive iron reaction (ammonium thiocyanate test) in evidence of mainly absorbed iron compounds on the surface of quartz. The surface films have also been observed on other minerals present in the system, e.g. zircon.

Sulphides occur in the heavy minerals to the extent of about 10% and are distributed across the gravity range. This is due to the fact that the sulphides are frequently associated with a few crystals of quartz, which changes the gravity of the aggregates. The amount of sulphide varies as indicated from sulphur analyses, illustrated in Table 3-18. A general trend observed is that both carbonates and sulphides appear to occur more in tact at the bottom of the formation. This may be due to more oxidation and removal of these minerals into aqueous solution under acid conditions that occur at the top of the formation by penetration of surface water containing dissolved air. Hence there is less evidence of these minerals in the top part of the marine formation. This is consistent with the tentative observation that poor processability tar sands contain in general less sulphides based on wt% of heavy minerals, and more degradation products of oxidation. Thus it may be interpreted that oxidation of sulphide has taken place and ions have gone into solution and been redeposited or adsorbed on surfaces, even eons ago. Further, these reactions can occur now due to sampling of disturbance of the formation e.g. blasting bulldozing.

Some carbonaceous fragments floated on top of bromoform. These particles and other carbonaceous fragments obtained from the sand phase after hot water separation, both exhibited negative zeta potentials of about 14 mv after crushing and suspension in water. They are also highly reactive e.g. H_2O_2 treatment of these fragments results in rapid oxidation frequently leaving what appeared to be fine silica under a microscope. It should be noted that both the heavy minerals and the carbonaceous fragments lose weight on ashing and hence, will affect ash determinations on separated solids.

3-4-1 Iron Reduced Minerals

The tar sands contain iron, that appears to occur mainly with the fines, i.e. water phase, froth solids. It has been found that the bulk of the iron is in the ferrous state. This was observed first in a 3 sectional electrophoretic cell. When mixing was stopped, sand settled to the bottom, a lens of clay was observed adhering to the diaphragm nearest the anode and a green material formed a

Table 3-15

Solids and Heavy Mineral Removal in Different Process Stages

Process Stages	Solids Removed Wt % on Total	Heavy Minerals Wt % on Solids Removed	Heavy Minerals Removal Wt %	Iron Content of Solids Wt %*
1. Water Washing	52.0	0.2	3.1	2.0
2. Varsol Dilution				
(a) Settled Solids	34.7	24.0	96.7	11.0
(b) Water Phase Suspn	3.6	0.4	0.02	8.5
(c) Emulsion Solids	5.6	3.2	0.2	8.0**
(d) Oil-Solvent Suspn	4.1	Nil	Nil	7.9**

* After heavy mineral removal
** Trace metals are high

lens at the diaphragm nearest the cathode, indicating it was a positively charged type sol. Removal of this green material and suspension in distilled water resulted in a fairly rapid change to red from the oxidation of ferrous and ferric.

Extraction of iron from tar sands with hot dilute HCl followed by filtering off the solids and oil, and neutralization of the filtrate resulted in the precipitation of green ferrous hydroxide. Not all the iron is removed by this technique, and results vary for different tar sands. The average amount removed by this acid extraction was about 30% of total iron measured by X-ray fluorescence. Great care was taken to eliminate air in these operations to avoid oxidation of ferrous to ferric.

Not enough work has been carried out for accurate comparative values on a wide variety of tar sands, and not all the iron is soluble even in concentration acid. However, preliminary data showed that the iron content of a good quality Area B type tar sand was essentially 100% soluble ferrous iron, whereas poor quality samples, Area D Hole 11, from nearer the top of the formation contained mostly ferrous iron with some ferric iron. The "bonded" iron state on the surface of minerals could play a significant role in the processability of tar sands.

Further work is indicated to determine the distribution and state of the iron in a range of tar sands, and verify that the main source is always sidente.

3-4-2 Sulphide Oxidation

The proposed mechanism of oxidation postulated is that water is lost by capillary action from the three dimensional connate water system formed by touching sand grains surrounded by films of water. Air is thus introduced in very minute bubbles into the capillary system. Oxidation of the sulphides can now take place.

It is well known that pure sulphide minerals do not oxidize as rapidly as minerals containing impurities. For example, in the case of sphalerite oxidation occurs as much as 10 times faster with pyrites present. As both pyrites and chalcopyrites are present in the tar sands and are probably impure, then the rate of oxidation of sulphides could be probably much greater than expected from literature values on pure sulphides. In the literature, oxidation of the sulphides have been reported to increase with increasing pH and the availability of oxygen.

The rates of oxidation appear to increase in the order, pyriteslchalcopyriteslsphalerite. The rate of oxidation of sulphides in alkaline media is indicated in the literature to be higher than that in acid media, and enormously increased by the presence of Ni or Mn in trace quantities. Thus the rate of oxidation of sulphides in alkaline tar sands would be high. The generation of acid by

Table 3-16

Gravity Fractionation of Solids from a Beaver Creek Froth Separated without Aeration*

Gravity Range of Mineral Fraction, g/ml	Wt % on Total Solids	Mineral Type
Colloidal	4.9	Gray Clay
-2.6	31.1	Carbon and Yellow Mineral
2.6 - 2.7	40.3	Fine Uniform Sand
2.7 - 2.96	8.6	Mica and V. Fine Heavy Minerals
2.96+	15.1	Heavy Minerals

* Using heavy solvent techniques and oil - water free, separated solids.

this process would overcome the normal alkaline pH of the tar sands resulting in an acid condition. The rate of generation of acidity will be a function of the amount of alkali, e.g. carbonates, present in the tar sand.

Chemical treatment of the heavy minerals was employed initially to detect the more reactive mineral species. A technique was used in which half a gram of separated heavy minerals from the tar sands was contacted with ten times its weight of both concentrated and dilute hydrogen peroxide or acid. A violent reaction occurred in most cases with hydrogen peroxide (30% solution) additions. After the initial violent reactions the solids settled out and it was possible to decant and filter the supernatant liquid. After evaporation, the amount of material that had gone into solution was obtained. With concentrated acid, treatment was carried out for a period of about 5 hours. Reaction was only very slight with acid. The results are inconclusive, silica appears to be solubilized by H_2O_2, and manganese by acid, Table 3-19.

Hydrogen peroxide converted sulphides into larger sized "limonite"? The colour of the limonite varies from almost yellowish-white through yellows to brown. For examples, a bright yellow to brown limonite is believed to occur from the oxidation of the brass-yellow sulphides, and a pink to reddish brown limonite with pink-red transparent crystalline incrustations are believed to result from the oxidation of the greyish-black sulphides, adhering to quartz grains.

More limonite is observed in good Beaver Creek heavy minerals after hydrogen peroxide treatment, perhaps less in the "intermediate", and least in the "bad" heavy minerals. Directionally, this agrees with the occurrence of sulphides. This is also paralleled by the appearance of considerably more limonite in the oxidized 29-16-2 bottom heavy minerals that those from Hole 11. Further the amount of soluble material from oxidation is higher for heavy minerals from good processability tar sands. This latter point is illustrated by the data in Table 3-20.

Identification studies of individual minerals were not carried out on these particular samples from these locations.

These observations tend to support the hypothesis that poor processability tar sands have undergone a degree of oxidation and corressponding ions have passed into solution. The ions going into solution were mainly iron with smaller amounts of aluminum, magnesium, titanium, manganese, silica and tin. A very positive test for sulphate using $BaCO_2$ was obtained with solutions.

An interesting observation was that oxidation also revealed many iron incrustations on the surface of the heavy minerals present. This observation may be important to an understanding of oil-solid attachment and flotation of the minerals.

Oxidation of an iron sulphide mineral will result in the formation of iron sulphates. In our oxidation studies with dilute hydrogen peroxide both tests for iron and sulphate have been very positive in all experiments with total heavy minerals, as well as sulphide type minerals which have been separated under a microscope.

Table 3-17

Opaque Heavy Mineral Sulphides and Carbonates

(i) Sulphides

The sulphides that occur are pyrites (FeS_2), chalcopyrites ($CuFeS_2$), and bornite (Cu_5FeS_4). Evidence has been obtained for the occurrence of sphalerite (ZnS), the amount appears to vary greatly with the location of the particular tar sand sample. The colours of these metallic like minerals are brass-yellow for pyrites (octahedral) and chalcopyrites (tetragonal) sometimes in well crystallined forms, brass-yellow with purple tarnished masses for bornite (small spherical crystalline masses) and whitish-grey for sphalerite (large crystalline masses). A greenish metallic sulphide highly reactive to oxidation also occurs in the Beaver Creek Area tar sands. Sulphides occur in sizes from very minute crystals or crystalline masses in in the size range of about 200 mesh, and up to larger masses of microcrystalline sulphides of about 20 mesh or greater in size. Very well-formed octahedron pyrites crystals have been observed. Often the sulphides occur as very small nodules attached to quartz or as films cementing quartz crystals together or adhering to their surface. Further, large masses of sulphides frequently have quartz grains attached to the outside and imbedded in the crystalline masses. Sphalerite (ZnS) has been observed to occur as a white to grey, metallic, crystalline mass.

(ii) Carbonates

The degree of occurrence of limestone or carbonates in the tar sands sample varies widely. Carbonates are present in most Mildred Lake samples as indicated by reaction to dilute acid. Their occurrence in most cases however are in the two main forms of either small single crystals, or amorphous masses or cement-like material bonding quartz crystals together into larger aggregates. Probably the most common of the carbonate is siderite ($FeCO_3$), Table 13 for general properties. Calcite and perhaps dolomite and magnesite (white crystals effervescing with hot dilute acid) have been observed to occur.

In general, the carbonates appear to occur more in the tar sands samples taken from the bottom of the deposit than from the finer grain tar sands taken from the top of the deposit, although this may be fortuitous. There is indication in the literature that siderite can occur in the tar sands in very large quantities up to as high as 15 wt%(7). The occurrence of carbonates in the Mildred Lake tar sand heavy mineral (> 2.963 g/ml) samples studied have been less than 1%, with the exception of 21A to date. On total solids, higher amounts could occur in the tar sands. This is because of an overlap in gravity (Table 13). It should be noted here that a complete isostructural series exist between calcite, magnesite, siderite and rhodocrosite(3). The formation of intermediate members of this series adds a complexity in the identification of which carbonates exist in a given sample.

It is interesting that the metal ions that occur most in solution in the tar sands are magnesium, manganese, calcium and iron (Section VII), all of which can occur as mixed carbonates in the tar sands. It is believed that the presence of carbonates even in very small quantities is very important to the separation of the tar sands in hot water separation as will be discussed in detail in Section IV B. Their contribution on the one hand adjusts and controls the pH of the system. However, on the other hand they contribute deliterious ions, which can affect the attachment of solids to naturally occurring oil surfactant and hence cause flotation of solids. A complete definition of the occurrence of carbonates has not been obtained, but should be studied further.

Carbonates appear in the heavy Beaver Creek Plant Feed heavy minerals to only a very small extent, generally <1% of the total heavy minerals. They have been observed as a few yellow-white and colourless crystals that effervesce in warm dilute HCl. However, more carbonates were found in Hole 21A and 29-16-2 bottom heavy minerals. Especially in 21A heavy minerals, appreciable yellow carbonates were observed to be present, which were estimated to be >10% of the total heavy minerals.

(iii) Others

There are minerals present which have not been identified. Many individual minerals have been observed, see summary Table 1, but they occur only as isolated grains. As a generalization some of these minerals are other members of the groups to which the major minerals belong.

Table 3-18

Sulphide and Carbonate occurrence in Heavy Minerals

Oil Sand	Processability	Sulphur (Wt %)	Wt % H_2O_2 Soluble	Effervescence with Dil. HCl	ΔpH (5 h)
A. Escarpment					
29-16-2 Bottom	Good	5.1	15	Large	+0.9
Hole 11	Bad	1.6	10	V. Small	-0.8
B. Beaver Creek					
Plant Feed	Good	4.4	25	Small	+0.2
Good	Good	5.5	33	Large	+0.2
Intermediate	Intermediate	5.5	15	Large	+0.5
Bad	Bad	2.8	10	V. Small	-0.5

Dilute hydrogen peroxide treatment has enabled the identification of most reactive species to oxidation, e.g. sulphides and siderite. The pH of a 0.6 wt% suspension in water of total heavy minerals extracted from Hole 11 tar sands was treated with 0.6% H_2O_2 solution. A decrease to 2.4 pH in a few hours occurred, and tests on the suspending media showed sulphate and ferric iron to be present in appreciable quantities. The pH also is similar to that of ferric sulphate, see Section 3-4-3. It was also mentioned before that other mineral species containing manganese were also very reactive.

Oxidation of the inorganics generating an acid condition and high salt content in the aqueous phase, strongly suggest that all precautions should be taken to avoid exposure of tar sands to the atmosphere to avoid water loss and oxidation. In a large commercial operation, the time between the exposure of the tar sands in the formation and the actual process operation would be reduced compared to laboratory storage of samples. Also, the effect of oxidation should be closely guarded against in laboratory experimental work. The best precaution here would be to use an inert gas blanket as well as cool storage at 35°F.

Another aspect of the effect of oxidation is in processing. Maintaining a reducing atmosphere and excluding oxygen could aid in hot water separation. Our studies have shown the application of a reducing system to the hot water flotation process to be difficult, and that even with inert gas in place of air any improvements were hard to measure. It may seem more reasonable not to take steps to use an inert gas system.

One concept that should be given consideration in the design of a commercial process is the use of minimum quantities of air at higher temperatures for flotation. This was adopted in Clark's original approach to hot water flotation process to minimize froth contaminants. Our findings substantiated that solids in the froth can be considerably reduced by eliminating the addition of air in at least the first stage of flotation.

3-4-3 pH Effects

Information has been obtained on pH and chemical addition in tar sand processing, but the origin of pH and the various interaction of ions in the tar sands and in the hot water flotation process has not been clearly evaluated. There is a basic chemistry that controls the system. Some of the reactions that are believed to occur are discussed below.

As the bulk of the minerals present have an extremely low solubility, the solution chemistry of these minerals does not apply to the process. Although the ion-exchange of some of the minerals may be quite important, only the small amount of minerals present which can be in equilibrium with corresponding ions in solution are chemically important.

Table 3-19

Soluble Material from Concentrated Hydrogen Peroxide and Acid Treating

Tar Sand	**29-16-2 B**	**Hole 11**	**---------------------------- Beaver Creek -------------------------**			
Heavy Mineral Source	**----- Bench Unit Froth -----**		**Plant Feed**	**Good**	**Intermediate**	**Bad**
			30% H_2O_2 Soluble			
Major >10%	Si,Fe	Si,Fe	Si,Te	Si,Fe	Si,Fe	Si,Fe
Large Minor 5-10%	-	-	-	-	-	-
Small Minor 1-5%	Ti	Al	Mg,Ti	Al,Sn	-	Al
Large Trace 0.5-1%	Mn,Mg,Al,Sn	Mg,Mn,Pb,Sn,Ti	Al,Mn,Ca,Zr	Mg,Ti,Mn	Mg,Mn,Sn,Cu,Ti	Mg,Mn,Sn,Ti
Small Trace <0.5%	B,Sb,Pb,Mo,V,Na Cu,Zn,Ni,Co,Ag,K Ca,Cr,Zr,Ce,Ti,U	B,V,Cu,Zn,Ni,Na Co,Ag,Ca,Cr Zr,Ti	Ba,B,P,Li,Pb Mo,V,Zn,Ni,Co Ag,K,Cr	Ba,B,Pb,Mo,V Cu,Zn,Na,Zr,Ni Co,Ag,K,Ca,Cr	Ca,B,Pb,K,Co	B,Sb,M,V,Cu Zn,Ni,Co,Ag,K Ca,Cr,Zr,Pb
Wt % on Total HY Min	15	10	25	33	15	10
			Concentrated HCl Soluble			
Major >10%	Fe	Fe	Fe	Fe	Fe	Fe
Large Minor 5-10%	Mn	Si	-	Mn	Mn	Mn
Small Minor 1-5%	-	B,Mg,Al,Ti,Mn,Ca	Mg,Si,Mn	Mg	Mg,Si,Al	B,Mg,Si,Al,Cu
Large Trace 0.5-1%	Mg,Si,Al,Ti,Ca	Ba,Cu,Zr	Sn,Al,Ca,Ti	Si,Al,Ti,Zr,Ca	Ca,Ti,Zn	Ca,Na,Ti
Small Trace <0.5%	B,Li,Pb,V,Cu Zn,Na,Ag,Zr,Co Ni,K,Cr	Pb,Sn,Mo,V,Zn Na,Ni,Co,Ag K,Cr	Ba,B,Li,Pb,Mo Zr,V,Cu,Na,Ni Co,Ag,K,Co	B,Li,Pb,V,Cu Na,Ag,Co,Ni K,Cr	B,Li,Pb,V,Na Ca,Ag,Co Ni,Cr	Li,Pb,V,Ag Zr,Co,Ni K,Cr
Wt % on Total HY Min	17	5	20	20	20	23

Table 3-20

Other Treatment Studies

Heavy Minerals from Beaver Creek	Wt % Hm on Total Solids	H_2O_2 Soluble	HCl Soluble
Plant	0.35	25	20
Bench #1(1)	0.64	5	10
Hole 21A(2)	0.32	15	25

(1) Acid poorer processability tar sand from top of formation
(2) High in carbonates (Siderite) and sulphides

When a mineral is immersed in water, a characteristic suspension pH of the mineral is established. The pH results from the interaction of water with the surface of the mineral. Some pH measurements of pure minerals suspensions were carried out and the results are summarized in Table 3-21. Two reactions are controlling:

- (1) absorption of H^+ or OH^- ions at the surface,
- (2) hydrolysis of the mineral

Quartz, silicates, aluminum-silicates and oxides are generally extremely insoluble materials. Hence, the first mechanism of H^+ or OH^- being the potential determining ions applies to these minerals i.e. the pH is determined by preferential absorption of ions on a dry surface. Thus, the charge and potential of the electrical double layer is determined by the magnitude of the pH.

Minerals that have a small solubility, establish an equilibrium with salts and ions in the water phase. These types of minerals are mainly carbonates and to a much lesser extent sulphides and some trace minerals such as apatite. The pH of the mineral suspension in this case is determined by the degree of acidity or alkalinity derived from the presence of the ions in the water phase. Hence a mineral composed of a strong base and a strong acid or conversely a weak base and a weak acid will in suspension will give an approximately neutral pH. However, if the mineral is comprised of a weak base and a strong acid or strong acid and a weak base then the pH will be acid or alkaline, respectively. This may be illustrated by simple equations as shown in the next table for a mineral = MA.

MINERAL REACTION IN SOLUTION		pH
$MA + H_2O$	$M^+ + H^+ + A^- + OH$-	7
$MA + H_2O$	$MOH + HA$	7
$MA + H_2O$	$M^+ + HA + OH^-$	7^+
$MA + H_2O$	$MOH + H^+ + A^-$	7^-

For example, calcite ($CaCO_3$) gives a strong alkaline reaction, and siderite ($FeCO_3$) exhibits a slightly acidic pH, Table 3-21. However, a higher partial pressure of CO_2 (bicarbonate formation) that is known to exist in in-situ oil sands can cause an alkaline pH. Sulphides tend to be neutral or acid and on oxidation result in distinctly acid media (~2.5 pH) resulting from the formation of iron sulphates from oxidation of pyrites, that hydrolyse to sulphuric acid.

An alkaline pH tar sand, therefore, appears to result from a simple excess of alkali and alkaline earth cations of weak acids in solution, or perhaps close to neutral pH when large amounts of siderite are present. Aging of tar sands is the result of oxidation of sulphides (pyrites) to iron sulphates, that hydrolyses to sulphuric acid and (neutralizing) the previous alkaline conditions. As the system becomes more acidic system the solubility of minerals, particularly carbonates, increase and hence the salt content of the water phase increases.

Table 3-21

pH of some Minerals in Aqueous Suspension

(0.6 wt % Mineral in Suspension)

Mineral	Formula	pH	Mineral	Formula	pH
Oxides			**Carbonates**		
Quartz (massive)	SiO_2	9.2	Calcite	$CaCO_3$	9.8
Sand	SiO_2	7.0	Dolomite	$CaMgCO_3$	9.5
Rutile	TiO_2	9.5	Magnesite	$MgCO_3$	8.9
Ilmenite	FeO, TiO_2	7.8	Siderite	$FeCO_3$	6.1
Silicates			**Fluorides-Phosphates**		
Garnet	$Mg, Al(SiO_4)_3$	10.0	Fluorite	CaF_2	6.6
Wollastonite	$CaSiO_3$	10.0	Monazite	$(Ce,La)PO_4$	7.7
Zircon	$ZrSiO_3$	9.4	Apatite	$Ca_5F(PO_4)_3$	9.1
Staurolite	$Fe_2Al_9O_7(SiO_4)_4OH$	9.3			
Kyanite	Al_2SiO_5	8.3	**Sulphates**		
			Barite	$BaSO_4$	6.8
Borates-Silicates			(Ferrous Sulphate)	$FeSO_4$	4.4
Datolite	$CaBSiO_4$	9.2	(Ferric Sulphate)	$Fe_2(SO_4)_3$	2.4
Tourmaline	$CaMgAl_6(BO_3)_3Si_6O_{18}(OH)_4$	8.6			
			Sulphides		
Clay Minerals			Pyrites	FeS_2	5.8
Kaolin	5.3				
Illite	(Variable)	2.9			

Note: Fresh distilled water used had a pH of 6.5.

It should be pointed out that this is an equilibrium system and that absorption on a surface of a mineral of other ions, such as H^+ or OH^- formed in hydrolysis of the mineral salt, can also take place. A result of this behaviour for certain minerals in suspension is that strong buffering properties are exhibited with little change from the characteristic pH with addition of acid or alkaline reagents. Only when an excess of one component in the system has been established will the pH change. It was interesting to note that in the case of tar sands that processed well, an increase in pH occurred. However, in tar sands that processed poorly, the pH showed a tendency to decrease with time. This general trend seemed to be paralleled by the presence of carbonates detected by their reaction with cold and warm dilute hydrochloric acid. The good processibility tar sands contained more carbonates in the heavy mineral fraction than the poor processibility tar sands. Although a complete carbonate content could only be obtained by fractionating the solids at 2.7 g/ml. In the case of Hole 21A, heavy

mineral where the carbonates (mainly siderite) are high, a pH of 6.5 was rapidly established. This directionally supports the above hypothesis as siderite exhibited a slightly acid pH. Further a tar sands containing calcite would exhibit an alkaline pH.

The measured values of pH for different minerals in Table 3-21, show that most minerals tend to establish a neutral to alkaline pH. This is normally characteristic of a tar sand sample. Hence, it is postulated here that the pH of tar sands is derived from the reaction of minerals, particularly carbonates with water present. It is interesting to note that the pH values for ferrous and ferric sulphate, are distinctly acid. The latter is hydrolized in solution to form sulphuric acid. For example, a 0.01N solution of sulphuric acid has a pH of 2.1. Iron sulphates are products of oxidation of pyrites. Both iron and sulphate ions have been detected by isothiocyanate and $BaCl_2$ precipitation tests in suspensions of total heavy minerals that have undergone even a small degree of oxidation, such as long standing at room temperature and also treatment with a dilute (0.2%) H_2O_2 solution. Thus oxidation plays a key role in pH changes to acid conditions.

The connate water of the tar sands varies, but an average value is about 5 wt%. Salts present in fresh tar sands are normally about 0.05 wt%. This indicates that the connate water (variable) in the tar sands is at least about a 1 wt% solution of salts in equilibrium with the minerals and clays present. It was shown before that on dilution with water the same characteristic pH is established for the particular tar sands in the hot water flotation process. This observation is quite consistent with recent work on individual mineral suspensions in which dilution of mineral suspension reestablishes a characteristic pH. It was concluded that this behaviour was not entirely due to the hydrolysis of the mineral salt. The increased pH at low percent mineral suspension was attributed to the adsorption of OH^- directly on the surfaces of other minerals but at higher concentrations it is transferred into solution upon dilution of the suspension.

Clean heavy minerals separated from different tar sand samples were placed in distilled water and the pH measured over a period of 5 hours. The results are shown in Table 3-22.

3-4-4 Clay pH Effects

pH measurements on slurries of tar sands with water prepared in the same manner have been found to vary from 3 to 9. If these slurries are screened through a 325 mesh sieve, the water phase was found to have the same pH. This is shown by the examples in Table 3-23.

Slurries of "clay" lenses (free of tar sands) in water have given variable pH measurements, similar to those exhibited by tar sands from the same areas, Table 3-24. Screening of the clay slurries through a 325 mesh sieve give the same results on the screened suspensions. When the material retained on the 325 mesh screen was washed with distilled water and redispersed, it exhibited a similar pH as that of the other suspensions. This indicates that the pH is a function of the state of the solids. This substantiates what is well-known, in that some minerals when added to water change the pH of the medium, e.g. calcite ($CaCO_3$) exhibit a pH of 8.

It has been pointed out that variability can be expected even within the same immediate area, so that this data should not be accepted as defining the pH of any given tar sand area.

pH values of H-kaolinite (4-5) and H-illite (3.5-4.5) are given in the literature. This suggests that adsorption of ions, e.g. Na^+ and/or polyvalent basic ions, on the surface of the clay have occurred to make them basic 8 pH. To raise the pH of H-kaolinite (m) and H-illite (m) suspensions containing 1-10% clay to 8 requires about 3 and 27 m. e.g. of NaOH per 100 g. This illustrates that kaolinite is a weak acid and illite a stronger acid.

The interesting point is that the ion exchange capacity of illite (and probably kaolinite) is increased 100-200% in aqueous solution when ions of polyvalent metals are adsorbed. The mechanism appears to be the formation of basic ions through hydrolysis, such as $Ca(OH)+$, $Fe(OH)+$, $Fe(OH)_{2+}$ or $FeOH^{++}$, which are adsorbed on the surface.

Mixing equal volumes of fines suspensions with very dilute acid and alkali solutions, about 0.0001N, gave only very small changes in pH. This "buffer" effect was clearly evident in titration curves for a number of suspensions of fines.

It should be noted that the concentration of an inorganic additive must exceed a critical limit dependent on the solids content before the pH condition can be altered appreciably. Also the high adsorptive capacity of the clay can result in flocculation with high salt concentrations.

3-4-5 Colloidal Material

Certain colloidal materials that bridge the gap in size between dissolved ions in the water phase up to 0.5m particles in the tar sands exist in small, but what might be significant amounts. The three main forms observed in the water phase are fine solids such as clay minerals, solubilized or emulsified oil, and colloidal forms of salt. The amount of all three colloidal forms increase in occurrence in alkaline media particularly above a critical pH of 8, which is about an average value for good processability tar sands. Precipitation of these colloidal materials occur under acid pH conditions. This may take place in the tar sand structure through oxidation generating an acid condition. Hence, some loss in processability may result through asssociation

Table 3-22

pH Changes of Heavy Minerals

Tar Sand Heavy Minerals	ΔpH in 5 Hours
29-16-2 Bottom	+0.9
Hole 11	-0.8
Beaver Creek	
Good	+0.2
Intermediate	+0.5
Bad	-0.5

Table 3-23

Water Phase Exhibits Same pH as Tar Sand

	pH	
Tar Sand Area	of Tar Sand Mixed With 80% Dist Water	of Water Phase Screened (325-) from Tar Sand Mix
B	7.6	7.7
D, Hole 9	6.4	6.5
D, Hole 11	4.7	5.2

Table 3-24

pH of "Clay" Varies

	pH		
"Clay" From	~10 wt % Total Solution	Screened Solution Through 325 Mesh	Washed 325+(2) In Dist Water
Area B Tar Sand(1)	8.8	8.5	8.4
A Core Lens (1 lb)	8.3	8.0	8.3
Area D, Hole 9 (in situ)(1)	7.9	7.8	7.3
Area D, Hole 9 Tar Sand(1)	6.7	6.8	6.7
A Large Lens (50 lb)	7.4	7.3	6.8
Hole 21A(1)	6.3	6.3	-

(1) Hand picked samples.
(2) Three washing through 325-.

of this material with oil interfaces, that is not readily regained with simple addition of inorganic chemicals such as sodium hydroxide in separation.

The pratical importance of sodium hydroxide addition is to increase dispersion of fine solids in the water phase that improves in separation. This effect however, will also tend to reduce the particle size distribution in the froth. Any dispersion in solid particle size in the froth will presumably have an effect in subsequent froth treatment, in that finer solids are now more difficult to remove from the water phase by centrifuging or settling.

Water phases from tar sand separations all gave little or no solids collected on a 0.45m filter. However, separations in alkaline conditions |8 pH resulted in dispersion of solids as measured by an increase in the amount of near colloidal material. Some results are recorded in Table 3-25. It should be noted, however, that greater dispersion of clay taken from clay lens, has not always resulted with pH adjustment to 9.5. Thus the variable "state" of dispersion in the system should be recognized.

The yellow colouration observed in the clarified water phases of .2m from tar sand separations with water at pH's of .3 was not due to the presence of oil, but to a colloidal suspension of inorganic material. The orange precipitate recovered was found through emission spectrographic analysis to contain mainly silicon and aluminum, with some iron in an approximate ratio of $FeSi_{10}Al_5$. This was considered to be more a "salt" than a suspension of clay minerals. The amounts recovered from separations of different tar sands are summarized in Table 3-26.

Colloidal salts were absent from the first washings of acid tar sands, such as "Bad" and "Bench No. 1". Other tar sands such as Unit Feed - Run No. 6 showed only small quantities of "colloidal" salt in the water phase. In general alkaline tar sands gave larger quantities of colloidal salt in primary water phases. The occurrence of this material indicates that although it is dissolved or suspended in alkaline media in the tar sand structure, it will be precipitated in situ with oxidation reducing the pH, or by acidification which was adopted in the laboratory technique. These observations suggest that silicate and aluminate ions are dispersed in the alkaline media (~8) of normal tar sands pH reduction causes these ions to revert to uncharged forms, e.g. $Si(OH)_4$, etc., thereby supersaturating the solution with eventual precipitation. This explanation is consistent with solubility of those materials in terms of pH and particle size.

The total precipitate of colloidal solids-bitumen-salt from the water phase with pH reduction could plate out on oil surfaces. This would render the oil particles more hydrophilic and more difficult to remove in Hot Water Flotation. Some "unrecoverable or permanent" loss in processability of certain "oxidized" tar sands have been observed previously. The precipitation effect described above may also explain why it is very difficult to regain processability, even with optimum alkaline treatment, with these types of tar sands.

In summary, some interesting observations on the occurrence of colloidal materials in the tar sands have been made. The effect of this material on the behaviour of tar sands as a function of pH changes and chemical addition requires further definition as this material could reduce bitumen recovery in hot water flotation.

3-5 Mineral Separation

In general, the flotation of silica, silicates, and aluminum-silicates can occur through either of three mechanisms:

- *(a) Absorption of polyvalent cations on the surfaces of the minerals which then act as a bridge for association with organic surfactants, i.e. specific groups attachment such as carboxylic anions and cations forming insoluble carboxylates; and*
- *(b) The accessibility of metal atoms in the surface layer providing a strong site for association with organic surfactants, which act as collectors for these minerals; and*
- *(c) The reverse to the above two alkaline processes, that is, an acid media with cationic collectors.*

Table 3-25

Solid Dispersion Increase with pH in Range 8-10

Beaver River Tar Sand		**Near Colloidal Solids(2), 0.8 - 0.45μ**		
	pH	**Wt % on Tar Sand**	**pH**	**Wt % on Tar Sand**
Plant Feed	8.2	ND(1)	10.0	0.070
Unit Feed - Run No. 6	7.4	ND(1)	9.6	0.064
Unit Feed - Run No. 9	8.1	ND(1)	9.2	0.050

(1) ND = not detectable by method used.

(2) No analysis has been carried out to date to determine the exact character of these solids.

Table 3-26

Colloidal Salt Decreases with pH

Tar Sand	**pH of Water Phases**	**"Colloidal Salt" (<0.2μ) Wt % on Tar Sands**
1. **"Aged"**		
Intermediate	8.5	0.168
Good	7.9	0.252
Bad	5.9	0.000
Bench No. 1	3.7	0.000
2. **"Fresher"**		
Unit Feed - Run No. 7	8.3	0.182
Unit Feed - Run No. 9	8.1	0.016
Unit Feed - Run No. 6	7.4	0.009
3. **"Plant Feed"**	8.2	0.057

Although these minerals show similar patterns of flotation behaviour, differences may result from different surface states (degree of ion adsorption, size, weathering, gravity, etc) and conditioning (pH and type of activating ion and organic surfactant adsorption).

As polyvalent ions both in solution and adsorbed or deposited on minerals exist in the oil sands, as well as normally occurring anionic surfactants under normal alkaline pH, and cationic surfactants under acid pH, then aeration should substantially increase the mineral content of recovered oil froth. Hence, it is not at all surprising that in the past when air has been used in both pilot plant operations and in laboratory separations that high solids content in the froth are obtained. Conversely, to minimize solids in the froth, aeration should be minimized in the separation process. Further, pH adjustment (NaOH) and suppression (polyphosphates, silicates) of mineral flotation in hot water flotation for oil recovery is of primary importance. This will be discussed in greater detail in subsequent sections.

The separation and recovery of heavy minerals is commercially practised with the black sands of Australia and of Florida. The separation process is complex and to be successful requires a feed that is a mixture of well formed grains preferably of reasonably similar properties. This is not the case for the heavy mineral suite in the oil sands. Hence, substantial effort would be necessary to develop a suitable separation process which may not be economically justified by the amount and quality of recovered minerals.

However, there is an incentive for this development in that over half of the heavy minerals are concentrated in the froth during Hot Water Separation, and these heavy minerals contain most of the zirconium and titanium.

In summary, it was concluded from these studies of tar sand minerals that in addition to other factors see Table 3-27, the "state" of the heavy mineral suite is an indicator of its original history as well as a rough measure of how well it will separate.

Table 3-27

Summary of Some Mineral Factors Affecting Oil Sand pH and Processability

- The sand is a fine-grained-quartz, mainly 30-200 US mesh in size. The particles are angular and have very small fractures or crevices. Sand is inert in separation processing.
- A small portion of the tar sand, estimated at ~1 wt % of samples studied, is composed of heavy mineral particles (2.9 g/ml).
- These heavy minerals were found to be distributed between the froth (60%) and sand (40%) in hot water separation, with none in the water phase.
- All the titanium and zirconium in these heavy minerals were found in the froth.
- The clay minerals identified in samples studied have been almost exclusively illite and kaolinite. This agrees with other findings in the literature.
- Clay lenses dispersed in water and fines suspensions screened from tar sands slurries exhibit different pHs.
- Titration curves are similar in shape for these suspensions, and show a significant buffering action of the clay minerals.
- The iron in the tar sands from near the bottom of the formation was present almost completely in the reduced state, i.e. , ferrous.
- Tar sands taken from the upper part of the formation contain some ferric iron indicating oxidation had taken place at some time.
- Ferrous-ferric oxidation may be a factor in pH reduction and 'aging' of tar sands.
- Not all the iron is readily soluble, and some appears to be strongly associated with surfaces of solids particularly in the clay fraction.

4

WATER

A premise of separation studies is that as water is the separating medium of solids and oil both in the tar sand structure and in processing, then all the physico-chemical properties of the surfaces will be related to the separating water phase. The amount of ions in solution will therefore have a profound effect on the system. This supposition is only partially true that will become apparent from the findings reported below.

There are several factors that determine the solubility of minerals and the amount of ions in solution in the connate water of the tar sands. The factors affecting solubility and hence processability are mentioned here to point out some of the considerations that must be made in exploring the chemistry of the oil sands. Measurement of properties of water phases from hot water separations with and without caustic and other chemical additives are also included in this section. These measurements were made for a better understanding of the flotation process.

Water analyses by soxhlet extraction with toluene that reject salts and colloids to the total solids on Mildred Lake tar sands have varied between 0.5 to 15 wt%. An average tar sand water content for a random number of samples was ~5 wt%. Connate water by soxhlet extraction of tar sands, as pointed out in Table 1-2, includes surface bonded water and unbonded water. The amount of free or unbonded water in the sample will vary depending on the particle size, Table 4-1, i.e. mainly the amount of clay and water. These literature data indicates that clay lenses are more saturated with water which is observed, Table 1-3, as a major portion of fines occur in clay lenses.

However, what is of importance in the water separation process is the water associated with the particle surfaces in the form of hydration films. The thickness of these surface films, or water of surface hydration, is dependent upon absorbed ions, pH, etc. This form of water is an important feed quality that is not measured directly and, of course, will be less than the total water.

Table 4-1

Capillary - a Function of Grain Diameter not affected b Drainage(39)

	αQuartz	Amorphous Silica	
Surface Energy	980	-	275±25
Heat of Wetting	564±16	-	142
Interfacial Surface Energy, ERGS/CM^2	416±	80 *	133±25
Particle Diameter (Millimicrons)			
α	0.0006	0.010	0.010
100	0.0007	-	-
50	-	0.011	0.011
10	0.0028	0.015	0.019
5	0.0120	0.021	0.035
3	0.0930	-	-
2	-	0.060	0.240
1	-	0.400	5.500
0.5	-	Essentially α	α

* Unpublished Observations

1. The solubility of a given form of silica varies with the particle size. This is shown by the equation of Ostwald-Freundlich modified by Dundon and Mack where S is the solubility of a large particule, Sr is the solubility of a particle of radius r, E is the surface energy in ergs/cm^2, V is the molar volume in cc, R is the gas constant 8.31 x 10^7 ergs/mole/degree, and T is the absolute temperature.
2. Quartz may be converted into amorphous sillca by grinding in water, which may have occurred in the oil sands to some extent.

Table 4-2

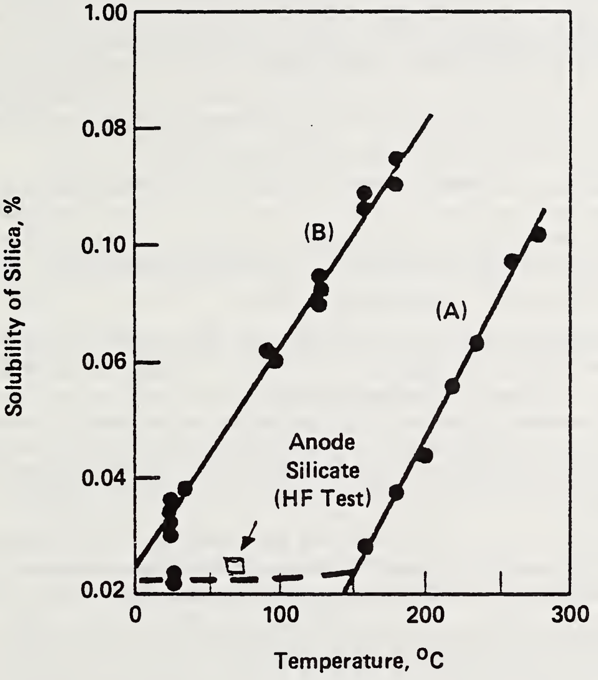
Calculated Solubility in Water at 25-30°C-%

Material In Column	Grain Size in mm	US Sieve	Max Height(1) In Feet of Water Column
Sands	2.0 - 0.05	8-250	2.5
Silts	0.05 - 0.005	325(3)	10
Clays	Less Than 0.005	-	30
Colloids	Less Than 0.001	-	-

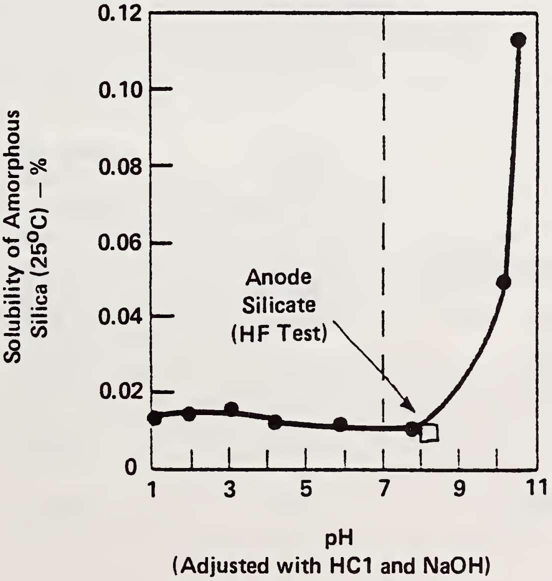
(1) Supported by Capillarity.
(2) Glass tube with and without vents at bottom of tube.
(3) Equivalent to about 0.044 mm.

Figure 4-1

Effect of Temperature on the Solubility of Quartz (A) and Amorphous Silica (B) (LIterature Data)



EFFECT OF pH ON AMORPHOUS SILICA SOLUBILITY



4-1 Salt Content

4-1-1 Mineral Solubility

Data on soluble salts in the oil sands is lacking. The bulk of the minerals are an inert group with very low, if any, solubility. Literature data on the solubility of an almost insoluble mineral, e.g. sand, is affected by temperature and pH, Figure 4-1, as well as particle size, Table 4-2, and crystal imperfections/impurities. For example, the solubility has been shown to decrease from 0.017 at 37°C to 0.003-0.0097% when alumina is present. Also, the addition of silica to a suspension of alumina depresses the solubility of alumina. The mechanism appears to be that of a insoluble alumina-silicate that is deposited at the surface of silica or alumina, preventing further dissolution. Metal ions could also precipitate as silicates.

Another important reaction is that of polysilicic acid (assumed to be similar to amorphous silica) with a metal ion. This is different from the reaction of a soluble silicate. The reaction may be regarded as an adsorption of the metal hydroxide ion on silica and is dependent on pH. In the range 2-3 pH, the absorption is strong. The reaction may be represented(15) by

$$\mathrm{SiOH} + (\mathrm{FeOH})^{2+} = (\mathrm{SiOFeOH})^{+1} + \mathrm{H}^{+}$$

The reversal in charge which takes place has been observed as well as the generation of hydrogen ions. For ferrous hydroxide ion, the pH of adsorption would be high ~8-9. Combination of the metal hydroxide with the polysilicic acid does not occur much below the pH at which the metal hydroxide is formed as a sol or precipitate. The combining capacity of silicic acid for metal ion decreases as polymerization of silica progresses. These reactions should also proceed with silica-alumina, perhaps to a greater extent because of the higher charge on the surface of these solids.

Although these types of reactions may have taken place in the oil sands, the main contributor to silicic acid is α quartz. This is based on electrophoretic studies of 8 pH oil sands that produced silicic acid (HF test) in the anode chamber equivalent to 0.0059%, Figure 4-1.

It should be noted that the combined effects of alkaline pH and small particle size could result in significant concentrations of silica in solution. The rate of dissolution would presumably be rapid and proportional to the surface area of the solid phase whereas from massive silica the rate would be slow, taking years. However, in the tar sands the silica has been in contact with films of water for thousands of years and it would be reasonable to assume that equilibrium has

Table 4-3

Soluble Salt Content of Tar Sands

Tar Sand Source **Feed Condition**	**Hole 11** **"Aged"** **(2 1/2 years)**	**Beaver Creek** **"Fresh"** **(a few months)**
Water Soluble Salts, Wt %	0.610	0.058
Major >10%	Mg,Fe,Ca	Na,Ca
Large Minor 5-10%	Mn	Al
Small Minor 1-5%	Al	Mg,Fe,Si
Large Trace <1%	Si,Cu,Na	Mn
Processability	Poor	Good
pH of Water Phase	2.5	8.0

been reached for the natural conditions in which a particular tar sand exists. This would suggest then that reactions involving amorphous silica, polysilicic acid and metal hydroxides which has resulted from the solubility and hydrolysis of carbonates, e.g. siderite, are complete and may be observed in the fine dust that is prevalent throughout the mineral suite, Section 3. Further, the measured pH of separated phases is indeed the characteristic pH of the in-situ water phase.

The solubility of carbonates and sulphides have been discussed before, Section 3, in terms of three effects of (a) CO_2 partial pressure, (b) oxidation of sulphides, and (c) complexing agents or adsorbents.

4-1-2 Soluble Salts

The soluble salt in a good quality Beaver River tar sand was found to be less than one-tenth of that in an aged "poor quality", escarpment Hole 11 tar sand. This comparison is shown in Table 4-3.

The low pH in the case of the aged tar sand indicated that oxidation of sulphides present, such as pyrites, had taken place. A very positive $BaCl_2$ test for sulphate substantiated this. An interesting observation was that the sodium is now a minor in Hole 11 due to the large amount of sol ions which have gone into solution from oxidation and a generated acidic condition. It is also important to note that the ions found are typically those found in "hard" water.

The value for good quality Beaver tar sands was about the same order of magnitude found by Clark[1] in his earlier studies, i.e. 0.05, 0.04 and 0.02 wt%.

The differences in salt content of oil sands was also observed from differences in maximum amperages attained in electrophoresis studies and electroendoosmosis effects. For example, 29-16-2 Middle and Area B gave maximum currents of 3-10 times larger than those for Holes 11 and 21A. This suggests that the quantity of soluble salts in these tar sands are different. Analysis of the anode and cathode liquids have shown significant quantities of Na, K, Ca, Fe, Cl, and SO_4 in 29-16-2 Middle. Area B showed the presence of appreciable silicate and HCO_3 or CO_3, as well as other ions listed above. Directionally, the magnitudes pesent were: Na> 5xK, Ca > Fe and Cl> SO_4. The absolute values are questionable as ion adsorption on the filters can take place. Estimates of the soluble salts in the samples studied were ~0.05 wt%.

4-1-3 Amount of Salts

A procedure was developed to measure more accurately the types of salts present, Appendix. The main disadvantage of this analytical tool is that operator judgment weighs heavily in the numerical results, so that a fair experience of technique is necessary before even semi-quantitative values can be obtained with confidence. However, in spite of this disadvantage emission spectrography is useful in deriving an approximation of the metal ions present in the clarified water phase. The results for salts from the eight different tar sand samples are shown in Table 4-4.

(a) Elements

The most predominant ion is sodium. Next are magnesium and calcium and to an even lesser extent iron and aluminum. The sodium appears in large amounts in all tar sands with the exception of Bench No. 1. The magnesium and calcium vary considerably between the tar sands; with more acid tar sands, which also gave the poorest processability values, containing a larger content of calcium and magnesium. All other elements observed are in much smaller quantities. It appears that "soluble" salt components may be related to pH and processability, through its calcium and magnesium content.

Under a microscope the dried and heated soluble salt appears to be a mixture of bright red amorphous forms admixed with more predominantly clear needle-shaped crystals. This varies from tar sand to tar sand and frequently black crystal forms are observed.

---

[1] *Clark, K. A., Pasternak, D. S. Ind. Eng. Chem. 24 1410-16 (1932)*

(b) "Colloidal" Salt

The amount varies with the type of tar sands and is frequently high, i.e. 0.1 - 0.2 wt%..

The main constituents of the "colloidal" salt are silicon and aluminum with some iron in a relative constant ratio, approximately $FeSi_{10}Al_5$. This is presumably related to the solubility of the oxides, e.g. silica.

In contrast to the "soluble" salt, the "colloidal" salt does not vary very much in colour which is usually beige or dull brown-white mass after heating. It appears to be the same from all the eight tar sands used in these studies. This suggests that colloidal salt is more or less of constant composition, and this is supported somewhat by the mass spectrographic results.

As a generality, the more alkaline the tar sands, the greater the amount of colloidal salt content would be expected.

(c) "Total" Salt

The amounts and semi-quantitative percentages of components on the "total" salt are given in Table 4-4.

(d) "Maximum" Salts

The "soluble" salt of different tar sands was found, however, to increase with increasing number of 1:1 washings of the tar sand, Figure 4-2. This suggests that the soluble ions in the water phase are in equilibrium with their solid state in the natural structure. Further, increasing the amount of water in the separation process will not necessarily dilute the soluble salt, as more of the solid salt will dissolve. That portion which dissolves after the first 1:1 wash is termed "solubilized", see Figure 4-2. The "maximum soluble" salt is therefore the sum of the "soluble" salt - representative of that salt present in a separation water phase - and the "solubilized" salt - that salt dissolving with further washing. An arbitrary number of 12 washings was taken as the point defining the "maximum soluble" and "maximum colloidal" salts.

The amounts and component concentrations of these salts are shown in Table 4-2. They are similar to just the "soluble" and "colloidal" salts in the number and kind of components. However, in general there appears to be a significant increase in the calcium and magnesium content in the "maximum soluble" salt. This suggests that these elements are present in relatively more soluble mineral or deposit forms.

(e) "Separations" Versus "Maximum" Salts

The relationship of the "maximum soluble" and "maximum colloidal" salts to those present in a single 1:1 washing, i.e. in tar sand "separation", are shown in Figures 4-3 and 4-4 respectively. Although, there is considerable scatter in the data from these eight different types of tar sands, an approximately similar amount of "solubilized salt" appears to occur in all cases.

It is very interesting that acid tar sands such as Bench No. 1 and "bad" tar sands gave zero "colloidal" salt in the separated water phase. This is consistent with the use of acid conditions to precipitate this portion of the total salt. However, further water washings resulted in "colloidal" salt extraction from these acid tar sands.

The implication of these observations is that when the natural pH of the tar sands is lowered by oxidation of inorganic sulphides to sulphates followed by hydrolysis to free sulphuric acid, then precipitation of colloidal salt in situ will occur. This precipitated salt may become associated with the surface of the oil particles rendering them hydrophilic rather than hydrophobic and therefore not as readily separable in Hot Water Flotation. The net effect, even with pH adjustment to optimum alkaline conditions can result in a permanent loss in processability. Minimization of tar sand exposure and working in air in commercial operation is again strongly recommended.

(f) Effect of pH

The effect of the pH of the wash solution on the amount of total salt removed in a 1:1 wash was observed to have an effect. A plot of preliminary data is shown in Figure 4-5. The salt content appears to increase with decreasing pH for all the types of tar sands investigated.

Table 4-4

Emission Spectrographic Analyses for Components of Salt Dissolved in the Water Phase

Beaver River Tar Sands (Designation)	Plant Feed	Good	Inter-Mediate	Bad	Bench No. 1	Unit Feeds - Run Numbers		
						6	7	8
A - Soluble Salt in Water Phase								
Salt, Wt % on Tar Sand	0.042	0.042	0.040	0.057	0.078	0.026	0.020	0.013
Components, Wt % on Salt								
Sodium (Na)	~25	~25	~25	~15	2	~15	~25	~25
Magnesium (Mg)	1	2	2	6	~15	10	7	8
Calcium (Ca)	1	1	1	3	7	10	3	10
Manganese (Mn)	0.07	0.07	0.07	1	0.8	0.7	0.1	0.1
Aluminum (Al)	1	1	1	0.2	0.8	1	3	0.7
Iron (Fe)	1	2	2	0.2	3	0.1	1	0.7
Silica (Si)	0.7	0.8	1	1	3	1	1	0.7
Others*	0.3	0.2	0.3	0.4	0.2	0.2	0.4	0.3
Total	~30	~32	~31	~27	~32	~36	~40	~45
B - Salt From Clarified Water Phase (i.e. Soluble + Precipitated)								
Salt, Wt % on Tar Sand	0.099	0.294	0.208	0.052	0.076	0.035	0.202	0.029
Components, Wt % on Salt								
Sodium (Na)	10+	4	5	~15	2	6	3	~15
Magnesium (Mg)	1	1	3	5	4	5	2	2
Calcium (Ca)	1	1	1	3	7	6	1	2
Manganese (Mn)	0.1	0.1	0.1	2	1	1	0.2	0.2
Aluminum (Al)	8	4	9	1	1	3	5	2
Iron (Fe)	3	3	7	0.5	3	2	2	5
Silica (Si)	~15	~15	~15	3	6	9	~15	~15
Others*	2	1	1	2	2	1	1	2
Total	~40	~29	~41	~32	~26	~33	~29	~43
C - Total Soluble Salt (Cum - 12 Washings)								
Salt, Wt % on Tar Sand	0.083	0.060	0.066	0.088	0.102	0.056	0.046	0.069
Components, Wt % on Salt								
Sodium (Na)	~15	~15	~20	~15	4	~15	~15	~15
Magnesium (Mg)	7	4	4	10	10	8	9	~15
Calcium (Ca)	3	3	6	~15	~15	7	7	7
Manganese (Mn)	0.7	1	0.2	1	0.5	1	1	1
Aluminum (Al)	1	1	0.7	1	1	1	1	1
Iron (Fe)	1	2	1	2	1	1	5	1
Silica (Si)	2	3	1	6	3	4	1	1
Others*	2	0.3	2	1	0.5	0.4	1	0.5
Total	~32	~29	~35	~51	~35	~37	~40	~42
D - Precipitated Salt (Cum - 12 Washings)								
Salt, Wt % on Tar Sand	0.096	0.389	-	0.154	0.0002	0.152	0.306	0.120
Components, Wt % on Tar Sand								
Silica (Si)	~15	~15	-	~15	-	~15	~15	~15
Aluminum (Al)	4	7	-	9	-	8	4	10
Iron (Fe)	2	3	-	3	-	7	3	3
Magnesium (Mg)	0.7	1	-	1	-	1	1	1
Sodium (Na)	0.2	0.3	-	0.3	-	0.3	0.3	0.7
Calcium (Ca)	0.2	0.3	-	0.3	-	0.2	0.3	0.5
Others*	0.5	0.3	-	0.2	-	0.2	0.2	0.2
Total	~23	~27	-	~29	-	~32	~24	~30

* Mainly: Boron, copper, lead, potassium, chromium and titanium.

(g) Specific Conductance

The specific conductance of the water phase was found to display a linear relationship to the soluble salt content of the water phase with the amount of "colloidal" salt as a minor parameter, Figure 4-6. The effect of "colloidal" salt which passes through a 0.2μ filter, is to increase the specific conductance for a given soluble salt content of the water phase. The increase however, is relatively small, substantiating that the precipitated salt present in the water phase is more in the form of a colloid.

(h) Sulphate Content Determines Acid pH

Qualitative measurements of the sulphate content of the water phase from different tar sands exhibiting different pH's gave a relation similar in the acid region to that of sulphuric acid, Figure 4-7. This tends to support that the original hypothesis of free sulphuric acid as the cause of decreasing pH generated by oxidation of naturally occurring sulphides in the tar sands may be correct. The slightly alkaline condition of the tar sands in the region of 8.0 - 8.5 pH was attributed to the presence of carbonates in the minerals. Preliminary data indicated carbonate to be present in about 1% concentration on salt. Chloride was absent in all samples tested.

Much work was involved in the development and evaluation of the salt content of the tar sand. It does not appear to be a simple or critical parameter. However, certain components of the "soluble" salt appeared to be far more critical than the total value. These, of course, are the polyvalent ions that contribute to "hard" water.

4-1-4 Summary

The accurate measurement of the salt content of tar sands has proved difficult, because of complicating colloidal phenomena. However, techniques have been developed which enable a measurement of the total salt content to be made in terms of "soluble" and "precipitated or colloidal" portions.

Soluble salts contain mainly sodium, calcium and magnesium ions. These latter ions increase in concentration with decreasing pH of the tar sands, and appear to be more critical parameters than the total salt content. This will be discussed in greater detail in Section 7.

Colloidal salts contain mainly silicon, and aluminum with some iron in a relatively constant composition. This portion of the salt is presumably related to the solubility of the oxides present in the tar sand minerals.

The soluble salt is indicated to be in equilibrium with solid forms. Thus, further dilution results in more "solubilized" salt going into the water phase. Decreasing the pH of the water washing phase resulted in larger quantities of dissolved salts being removed into the water phase by the technique. The soluble salt is related directly to specific conductance with parameters of the amount of "colloidal salt".

Sulphate content of the soluble salt increase with decreasing acidity of the tar sands. This tends to support the theory that oxidation of metal sulphides to sulphate followed by hydrolysis to free sulphuric acid which results in an acid pH is the mechanism of aging. However, the precipation of colloidal material in acid media may result in association of this colloidal material with the hydrophobic surfaces of oil particles rendering them hydrophilic and not readily separated in Hot Water Flotation. The net effect even with adjustment of pH to optimum alkaline conditions can result in a permanent loss in processability.

Minimization of exposure of tar sands to air in a commercial operation is strongly recommended.

4-2 Polyvalent Ions

4-2-1 Mg and Ca Determinations

The details of titration techniques for magnesium and calcium are reported in Appendix. Certain ions, i.e. Fe^{+++} = 20 mg/P, Fe^{+++} = 20 mg/P and Al^{+++} = 5 mg/P were cited in the literature as interfering ions in the titration. Thus, the original reason for clarification of the water phase in splitting the total salt into "colloidal" and "soluble" portions was to eliminate most of these interfering polyvalent ions from the clarified water phase.

Figure 4-2

Examples of Water Washing Tar Sands

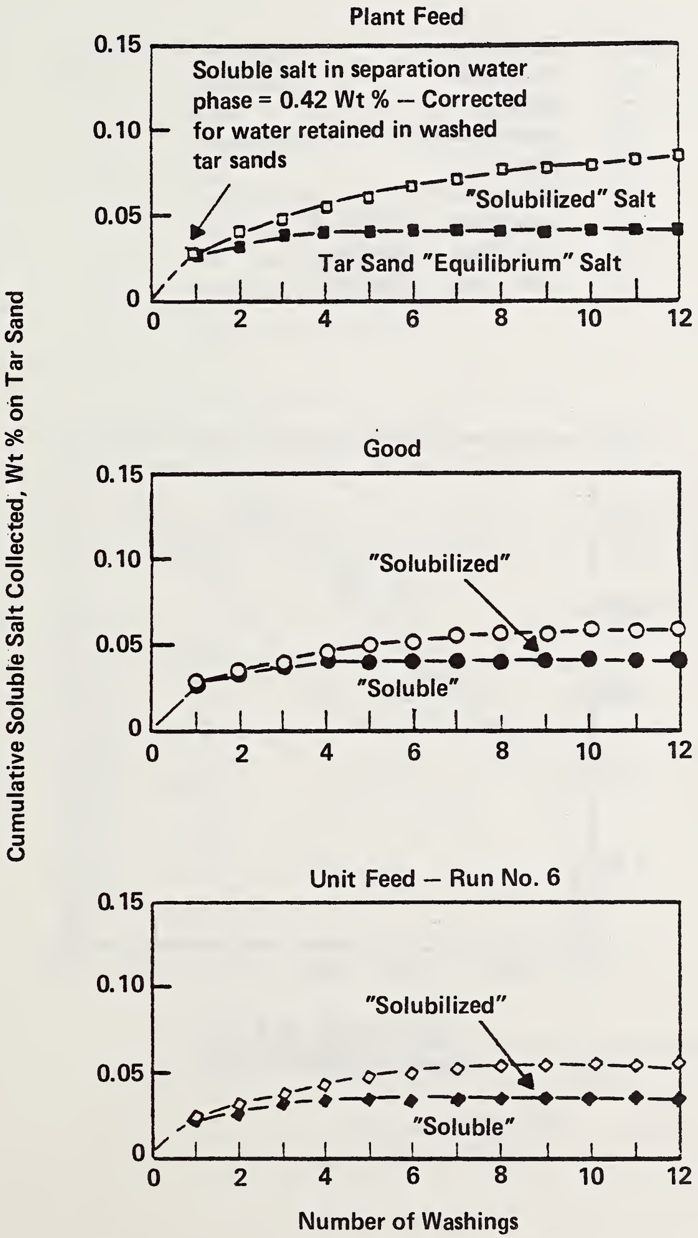


Figure 4-3

Effect of Number of Washings on Soluble Salt Content

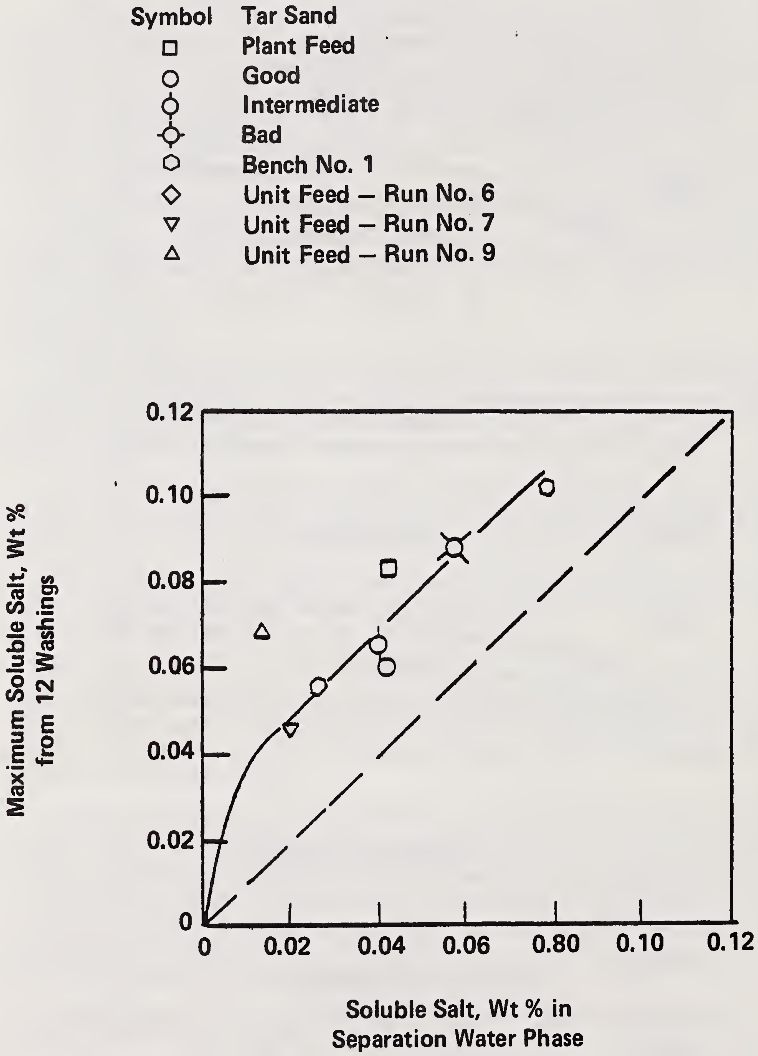


Figure 4-4

Effect of Number of Washings on Colloidal Salt Content

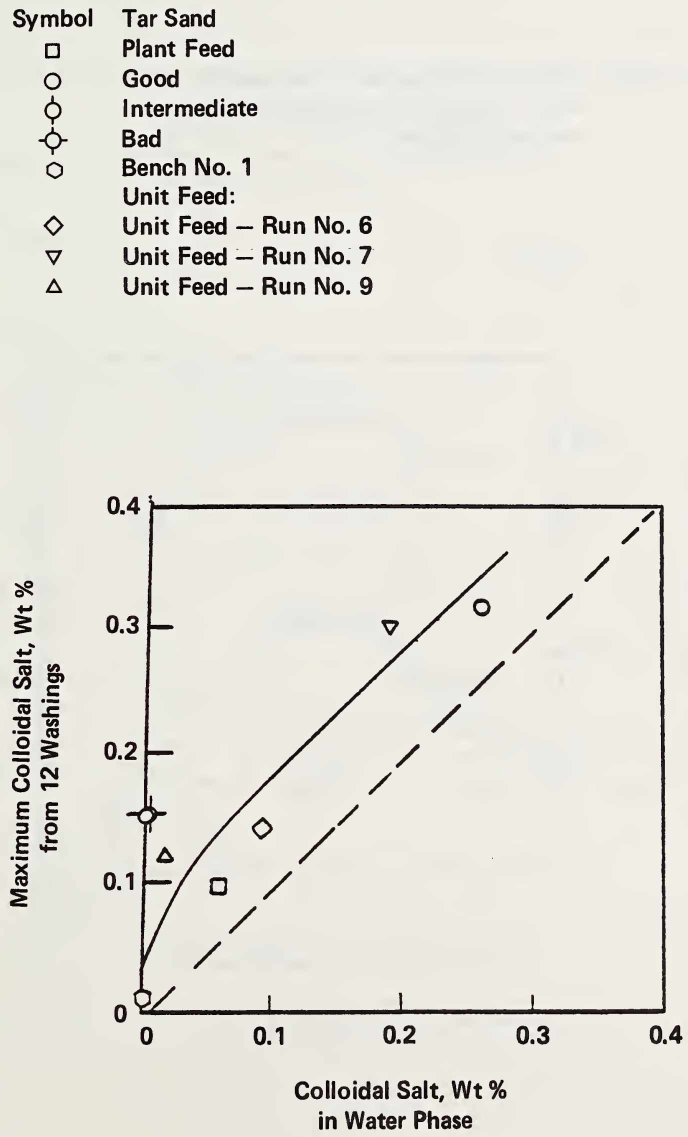


Figure 4-5

Salt Content Increases with Decreasing pH

Note: Values were obtained by subtracting amount of sodium hydroxide used from total salt collected

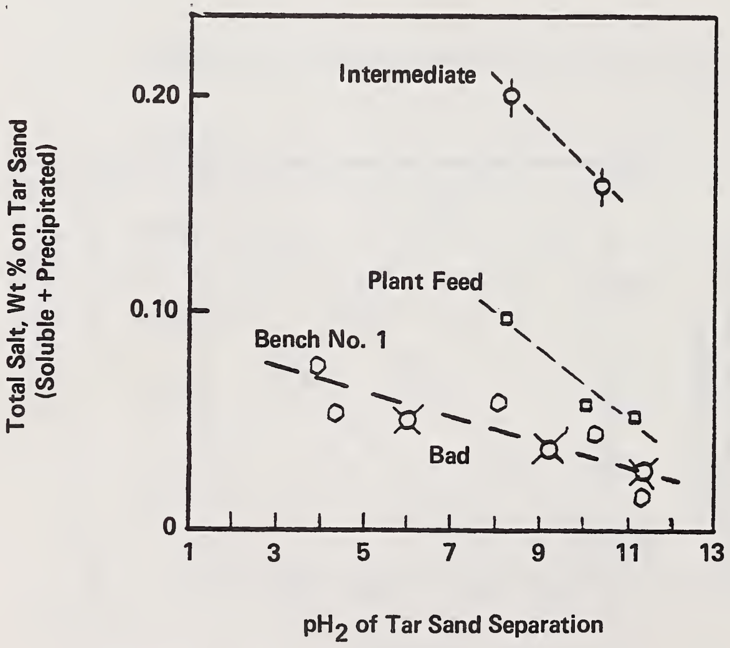


Figure 4-6

Effect of Soluble Salt and Precipitated (colloidal) Salt on Water Phase Conductance

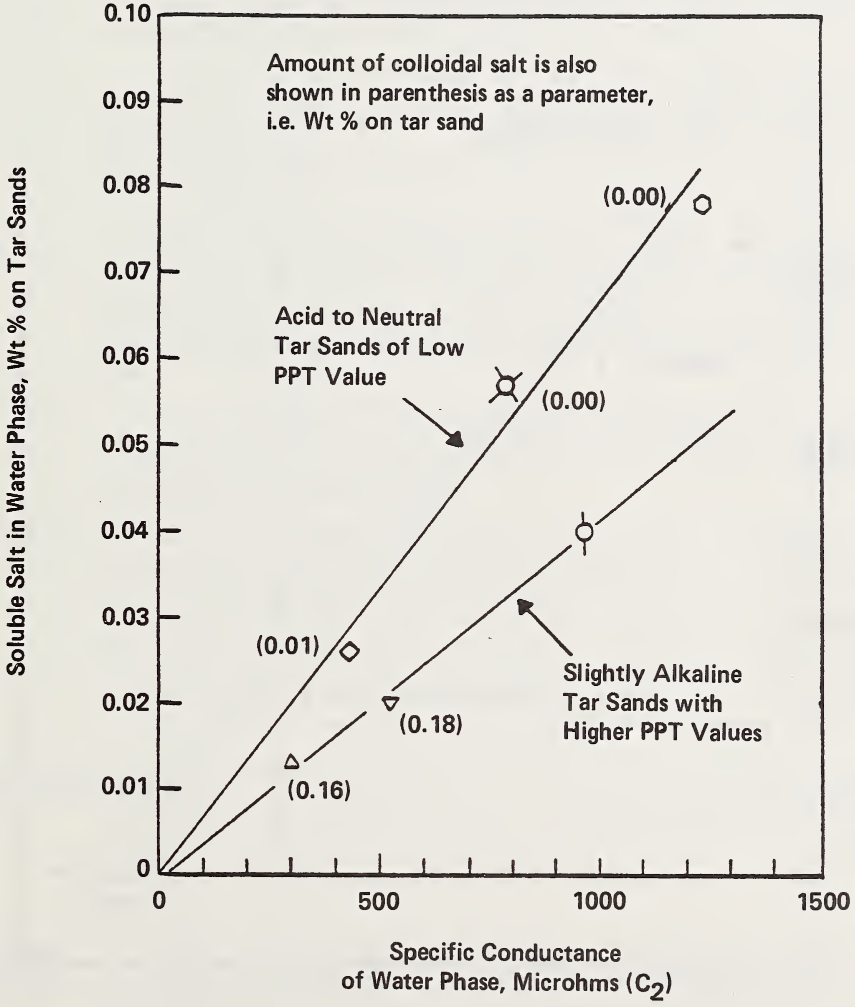
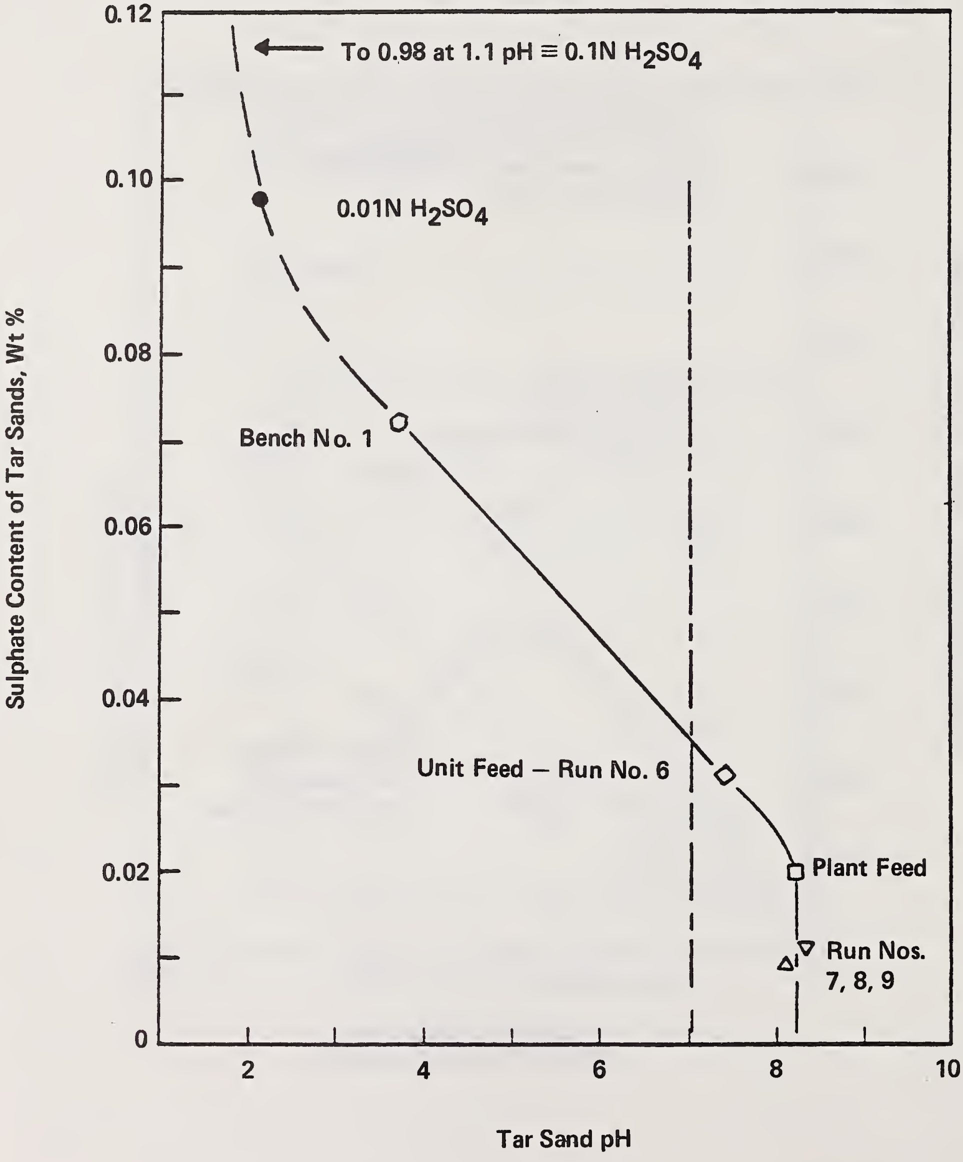


Figure 4-7

Free Sulphuric Acid from Oxidation of Metal Sulphides and Hydrolysis of the Resulting Sulphates Procedures Tar Sand Acidity



Thus, this study started with the preparation of clarified separation water phases containing only "soluble" salts. Titrations to obtain accurate concentration measurements of Mg and Ca pesent, using ethylenediaminetetracetate (EDTA) were carried out on these clarified water phases. The techniques and calculations of result are summarized in Appendix.

(a) Development of Techniques

Considerable difficulty had originally been encountered in reproducibility and accuracy both with and without "colloidal" salts. These difficulties were first attributed to the presence of interfering ions such as aluminum and iron etc., in the separation water phase. However, it was found that the variability in results was more a function of sample size. The latter had to be greater than 5 ml, as is illustrated in Figure 4-8. Although end points were not always obtainable with samples larger than 5 and high in concentration, e.g. water phase from Bench No. 1 tar sands. This anomaly was not followed up in terms of test limitations.

Further, it was found that the presence of interfering ions up to about the same concentration of the calcium being determined (~300 mg/l) did not seriously affect the accuracy of the end result, Figure 4-8A. Factors of determined values to actual concentrations of calcium and magnesium content as a function of concentration level and sample size were developed from the data, see Figure 4-8B.

An alternate to the use of factors was to treat all data graphically. This tends to give greater confidence in the final extrapolated determinations of calcium and magnesium in unknown water phase samples. Examples of this type of treatment are shown in Figure 4-9 for different tar sands. It will be noted that the same general curve, with sample size was found as shown in Figure 4-8 with synthetic solutions. Calcium determinations are very consistent. Fairly good extrapolations of total magnesium plus calcium values were also obtained by this preferred technique.

It should be noted, however, that determinations for just magnesium are difficult requiring precipitation of calcium as oxalate, which does not always occur to completion. Satisfactory development of a good reproducible technique for magnesium that could be used on clarified water phases has not yet been obtained.

(b) End Points

The normal end point of the titration is a sharp change in colour from red to purple for calcium, and red to blue for total Ca plus Mg. When sodium hydroxide is added to the system, the end point frequently becomes one of conversion of red to a purple colour in the total determination rather than blue. This was due to the formation of a red precipitate. Again, with certain types of tar sands, such as Intermediate, the end point is one of a colour change from red to green, when sodium hydroxide had been added. These end points are reproducible and have been used in the determination of calcium and/or magnesium content in the few cases when they occurred. As the occurrence is infrequent no effort has been made to explore these anomalies.

(c) Accuracy of Determination

A sample containing 300 mg/1 of calcium and 308 mg/1 magnesium, or combined giving a total of 608 mg/1 of these polyvalent ions, was tested by 31 laboratories. The published results gave a standard deviation of ± 13.7 mg/1 (~2%). In individual laboratories, standard deviations were about ± 3 mg/1 (0.5%). This data suggests that fair accuracy using this titration technique may be obtained. This was substantiated by fairly consistent results obtained in our exploratory studies.

(d) Development of Titration Technique

Further development of the titration technique for soluble ion concentration measurement and control of a commercial separation process for the Athabasca Tar Sands is strongly advocated. Such a development should investigate systematically and thoroughly these observations on a wider variety of tar sands. Prior to this, the development of a continuous preparation technique for a small sample of clarified separation water phase from continuous operations is required.

Also the use of a calcium-ion electrode, such as that devised by the Orion Research personnel and marketed by Fischer in conjunction with their expanded-scale pH meter, may prove a useful control technique. Evaluation of this type of electrode in the separation phase without clarification are other points to test in the development to avoid unnecessary work to attain the

Table 4-5

Effect of pH , Temperature, and Time on Precipitation of Calcium and Magnesium Hydroxides

Time Hours	Temperature °F	pH(1) of Sol'n	Calcium mg/l
$CaCl_2$ (390 mg/l)			
0.2	72	3.8	390
"	"	11.3	379
"	"	11.9	379
0.5	180	3.7	380
"	"	8.8 (7.3)(2)	379 (373)
"	"	9.3 (9.3)	368 (370)
"	"	10.2 (10.8)	379 (368)
"	"	10.9 (11.2)	265 (303)
"	"	11.6 (11.9)	108 (195)
3	"	11.9	216
0.5	200	8.6	400
"	"	11.7	70
$CaSO_4$ (410 mg/l)			
0.5	72	10.2	411
"	"	11.5	390
"	"	12.1	379
1.0	"	3.7	420
"	"	10.3	406
"	"	11.8	400
"	"	12.6	390
0.5	180	9.4	411
"	"	11.1	303
"	"	11.9	173
"	"	12.1	119

(1) Solution pH was adjusted with NaOH or HCl addition prior to standing time shown

(2) Values in parenthesis was obtained on Sol'n in contact with 2 Wt % bulk extracted oil dispersed in solution by high speed agitation.

information required for control. The accurate measurements of calcium and magnesium content in the water phase using these electrodes is presently being evaluated at Sarnia. Sulphate electrode for determination of the amount of inorganic oxidation and sodium electrode for measurement of Ca + Mg/Na ratio are also being evaluated.

4-2-2 Ion Concentrations

A number of titrations in the development of the technique were carried out to illustrate the effect of pH on precipitation of calcium hydroxide at different conditions of pH, temperature, and contact time. Some of these titrations were carried out in the presence of bulk extracted oil.

The results are tabulated in Table 4-5 and plotted in Figure 4-10. It can be seen that in general, only at high pH's (~11), at high temperatures (~200°F), and with long contact times is calcium precipitated from solution as hydroxide. Even then the remaining concentrations of calcium in solution are far higher than found with alkaline tar sands. The solid points representing experiments in the presence of dispersed bulk, solvent-extracted, Beaver River oil gave no relative change in calcium concentration to experiments without oil.

Thus any changes in concentration and magnesium ions in solution is not due to either precipitation of calcium hydroxide or interaction of these ions with dispersed bulk oil. It should be noted that the solvent extraction method of bulk oil recovery had excluded the naturally occurring water soluble surfactants with the discarded water and solids from tar sands.

4-2-3 Anion Effects

A comparison between the different sodium additives used in our studies is shown below.

Table 4-6

Only Tripolyphosphate Sequesteres Calcium

Sodium Additive	pH of Solution	Calcium* Determination, mg/l
None	6.1	43
Hydroxide	12.1	41
Carbonate	11.0	40
Silicate	12.1	37
Tripolyphosphate	9.9	0

* Actual concentration was 40 mg/l

Only the tripolyphosphate effectively complexed calcium, Table 4-6. The action of hydroxide, carbonate, and silicate in separation is therefore primarily one of pH change. This also applies to tripolyphosphate, which through its buffering action controls the pH near optimum. The combination of calcium sequestration and optimum pH control functions of polyphosphate was cited in the past as the reason for superior results with this additive, particularly in separation with aeration and poor quality tar sands.

4-2-4 Separation Water Phases

Clarified water phases from tar sand separations with water or solutions of acid and alkali in mixing were obtained for calcium and magnesium determinations. These studies were directed at observing any changes in ion concentration that might occur with pH. The results using the different tar sands under study and are plotted in Figure 4-11.

Figure 4-8

Effect of Sample Size, Interfering Ions and Sodium Hydroxide Addition in Titrimetry for Calcium and Magnesium Using Edta

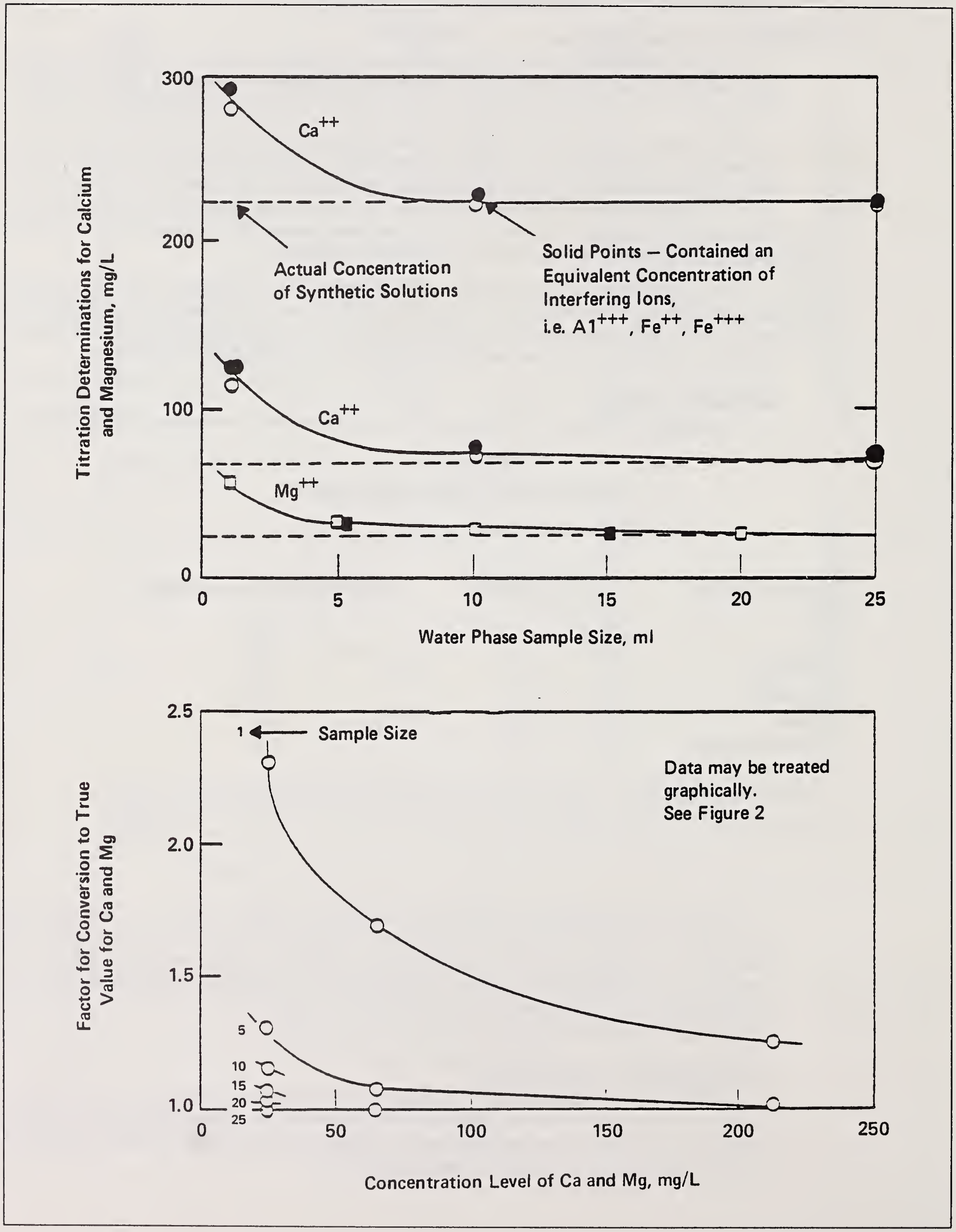


Figure 4-9

Determination of Calcium and Magnesium Ion Concentrations in Water Phases Using Ethylendiamine Tetraacetate Titration

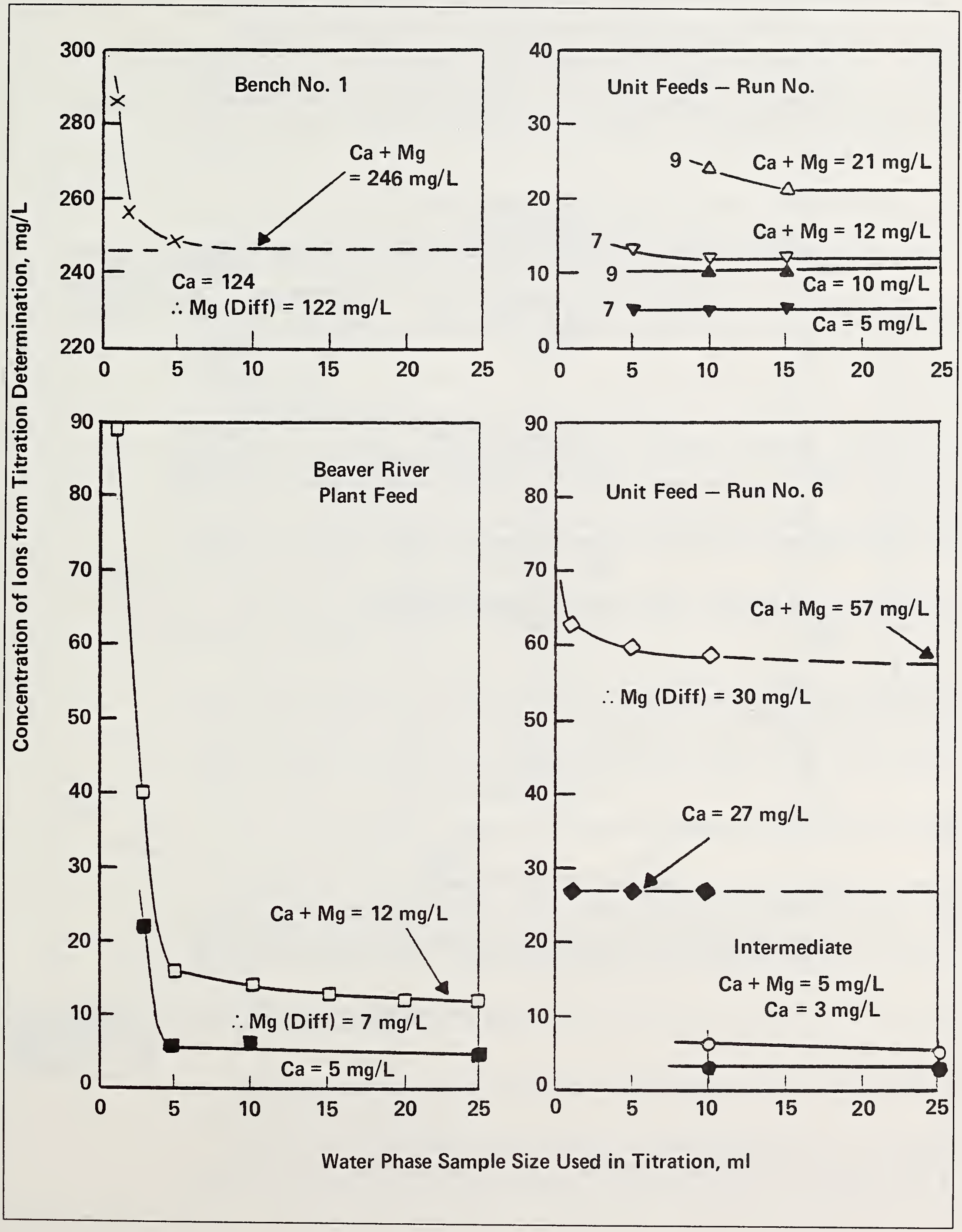
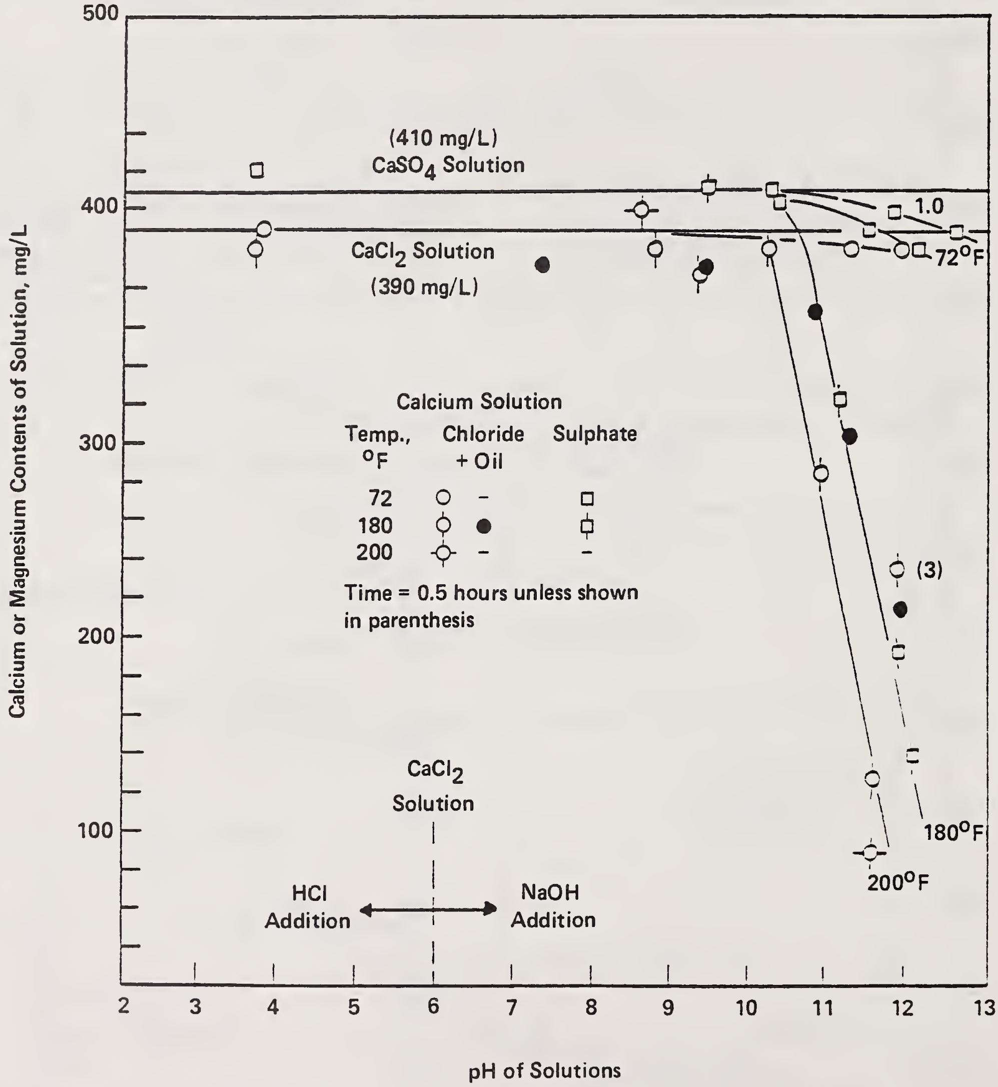


Figure 4-10

Precipitation of Calcium and Magnesium Occurs Only at High pH, Temperature and with Longer Contact Times



A most interesting and significant result was found. The data described a curve of high values in acid media passing through a very low minimum of calcium and magnesium content of the separated water phase in the region of 8-10 pH and increasing slightly at higher pH's than 10. The shape of this curve is the inverse to pH processability curves as measured by oil recovery.

The data indicates that in acid media both calcium and magnesium mineral forms are preferentially dissolved or desorbed from surfaces. These occur approximately in a 1:1 weight ratio. Hence, when oxidation of tar sands occurs, i.e. conversion of metal sulphides to sulphates followed by hydrolysis yielding sulphuric acid, an acid condition is generated resulting in increased amounts of calcium and magnesium ions in solution. This can also be seen from the data on the separations of different tar sands with only water, i.e. no additive, recorded at the top of Table 4-7.

It is indeed most interesting that adjusting the pH_2 to an alkaline condition results in a minimum of calcium and magnesium ions present in solution in the water phase. These ions are being taken up in an insoluble form. This insoluble form has been postulated before to be the calcium and magnesium salts of naturally occurring surfactants.

Therefore the shape of the curve in Figure 4-11 would be similar to the ionization-association of the polar groups of the surfactants. Another "insoluble form" for these ions would be "adsorbed" in flocculated clay.

4-2-5 Summary

The findings discussed on the pH versus Ca and Mg ion concentration of the water phase illustrate that the similarity between the behaviour of different tar sands in flotation may be governed by very selective chemical mechanisms. Hence, measurements of the concentrations of these ions in the separation water phase will be a factor in the control of a commercial operation.

It has been found that calcium and magnesium contents of the separation water phase vary with pH, or, conversely the pH of separation controls the calcium and magnesium content of the separating water phase. This is an unexpected finding.

Calcium and magnesium mineral forms are preferentially dissolved in acid media. Therefore, these ions occur more in "aged" (oxidized - acid) tar sands, as well as acid controlled separations of alkaline tar sands.

These ions could be removed from solution by the formation of insoluble carboxylate compounds, (e.g. membranes) with naturally occurring, at least partially water soluble surfactants from the oil in alkaline solutions. Therefore, the change in ion concentration with pH may also describe the ionization-association curve of the surfactant polar group or groups in the formation of these insoluble calcium and magnesium salts. This type of reaction may also be accomplished with certain additives, e.g. sodium tripolyphosphate.

However, it should also be noted that calcium and magnesium can exist in other "insoluble forms", i.e. adsorbed in flocculated clay.

The change in ion concentration with pH is the inverse of the processability curve as measured by oil recovery, which gave a small maximum at about 8-10 pH. This implies that measurement of calcium and magnesium contents of the clarified separation water phase could be used together with pH in control of processability of tar sands being separated in a commercial plant.

4-3 Separations With Additives

4-3-1 pH in Separation

The relationships of various pH measurements on the separation water phase from different tar sands, are shown in Figure 4-12.

The pH, of the water phase, without separating the suspended solids, is essentially equivalent to that of the clarified water phase including all washings used in separation (pH_3) and the clarified separation phase (pH_2). This is a useful finding in that the straight measurement

Figure 4-11

The Amount of Soluble Calcium and Magnesium in the Separation Water Phase Varies with pH

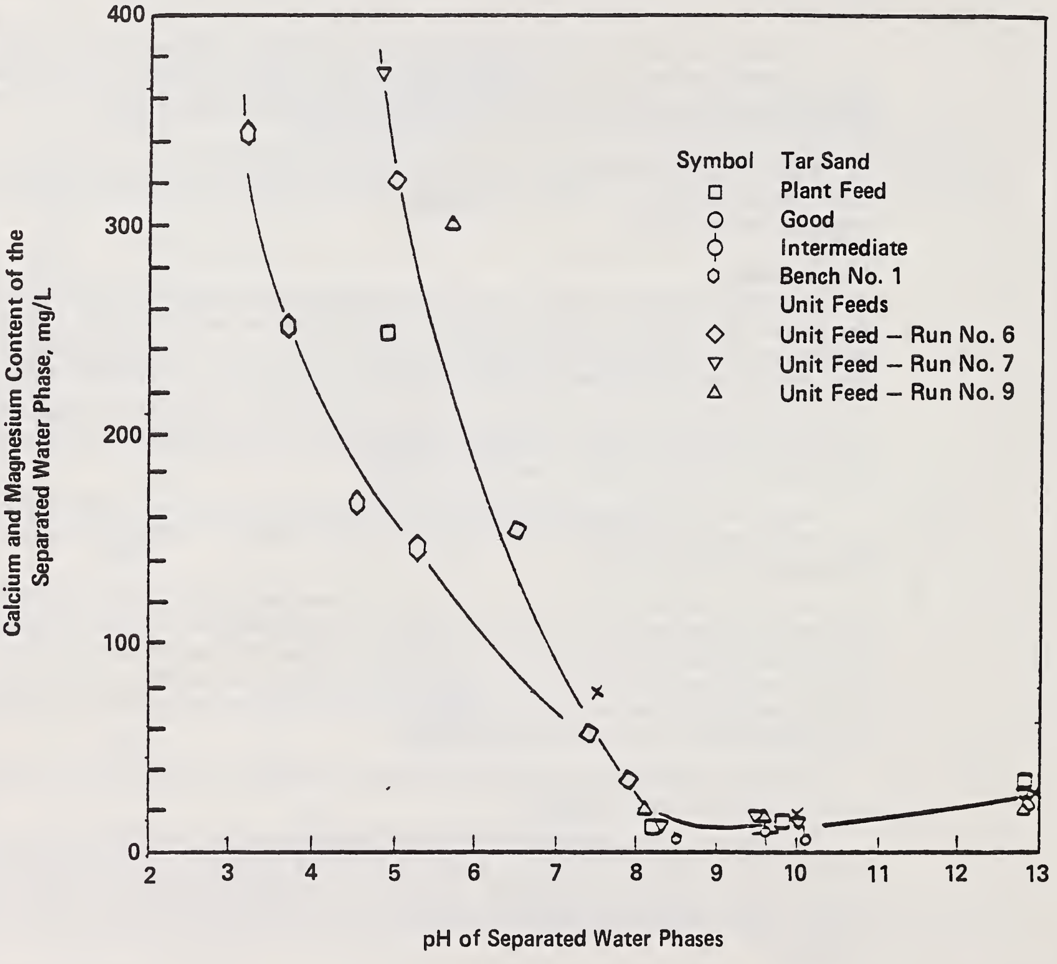


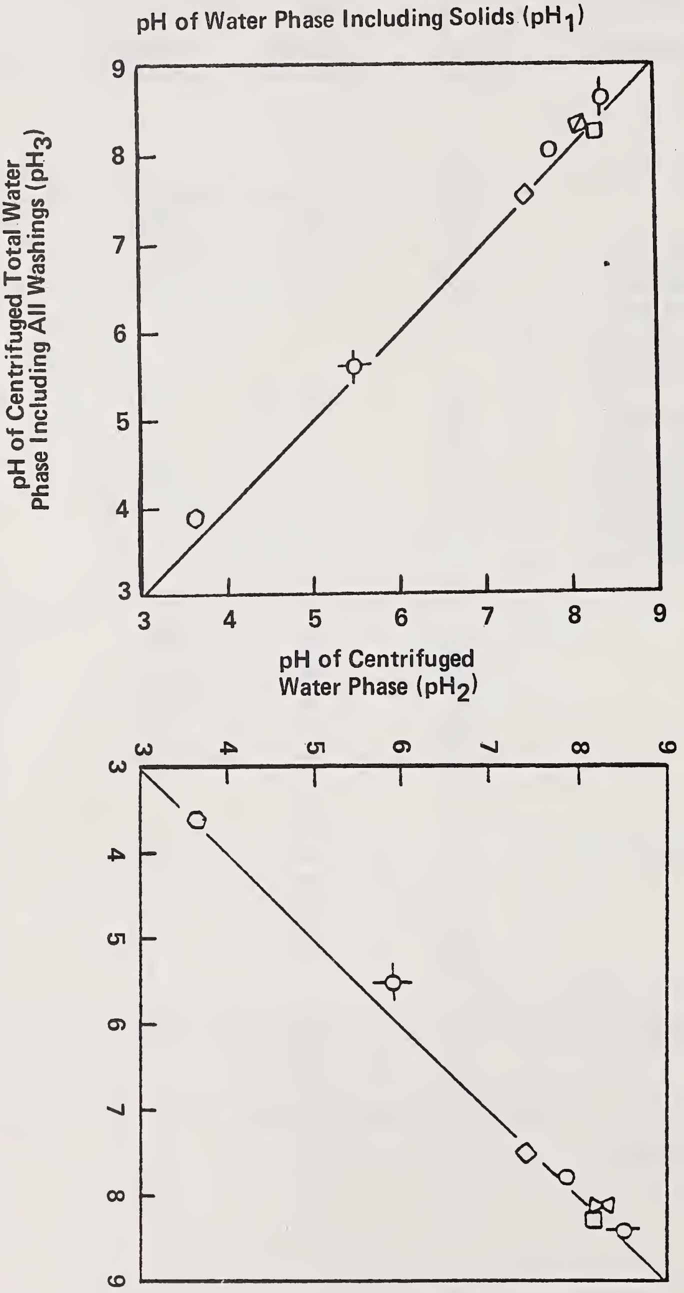
Table 4-7

Magnesium and Calcium Content of Separated Water Phases as determined by Ethlenediamine Tertraacetate Titrations

Beaver River Tar Sands (Designation)	Water Phase, pH	Calcium (Ca = mg/l)	Magnesium (Mg = mg/l)	Total (Ca + mg/l)
No Additives				
Plant Feed	8.2	5	7	12
Intermediate	8.5	3	2	5
Bench No. 1	3.7	124	121	245
Unit Feed - Run No. 6	7.4	27	30	57
Unit Feed - Run No. 7	8.3	5	7	12
Unit Feed - Run No. 9	8.1	10	11	21
NaOH or HCl Additive				
Plant Feed	4.9	97	151	248
"	9.8	5	9	14
"	12.8	11	23	34
Intermediate	10.1	3	3	6
Bad	9.6	4	5	9
Bench No. 1	3.2	162	181	343
"	4.5	92	74	166
"	5.3	76	66	142
"	7.5	42	34	76
"	10.0	10	6	16
"	12.8	16	13	29
Unit Feed - Run No. 6	5.0	184	135	319
"	6.5	80	75	155
"	7.9	16	20	36
"	10.0	6	5	11
"	12.8	11	11	22
Unit Feed - Run No. 7	4.8	108	263	371
"	9.5	6	10	16
"	12.8	11	15	26
Unit Feed - Run No. 9	5.7	135	164	299
"	9.6	7	9	17
"	12.8	11	13	24

Figure 4-12

Relationships of pH for Different Water Phases



(See Figure 68 for symbol on Tar Sand Designation) of pH on a typical water phase slip stream from a commercial separation unit may be used to obtain an accurate pH measurement on a continuous basis. Clarification of the water phase to remove fine solids, although not essential may also be used. Dilution of the water phase results in only very slightly reduced values indicating that the pH of the water phase is buffered by naturally occurring salts in solution. Further, the solids are in equilibrium with the water phase, and therefore do not effectively contribute to these pH measurements.

(a) Additive Solutions

As various solutions of different sodium salts at different concentrations have been used in separation studies data on specific salts used in terms of molality, specific conductance and pH was obtained, Table 4-8. Conclusions of the data are shown in Figures 4-13, 4-14, 4-15, and 4-16.

Sodium salts used, i.e. tripolyphosphate, carbonate, silicate, and hydroxide exhibit in this order, decreasing specific conductance and fairly constant pH with increasing molality, above about .005. These relationships have been combined together in Figure 4-15, illustrating that the pH of separation including chemical additions of sodium salts will not necessarily reflect the reaction of the additive, but rather that of a constant buffered pH. For example, sodium tripolyphosphate gives approximately optimum pH's for processability of about 9.5 ±1 at all concentrations.

(b) pH Versus Specific Conductance

The curves in Figure 4-16, for water phases from Hot Water separations, are similar but show a displacement toward neutrality compared with those in Figure 4-15 for the solutions used in separation. This indicates that some chemical reaction took place in separation with the addition of these sodium salts.Thus pH is dependent on the type of salt added, but is independent of the amount of salt added and the specific conductance of the water phase.

The effect of aging (oxidation) is also indicated in Figure 4-16. Directionally, the result is only a small change in specific conductance, but a large change in pH. This implies the generation of a small amount of a strong acid (sulphuric) consistent with the proposed theory of aging (oxidation) of tar sands.

4-3-2 Zeta Potential and Specific Conductance

(a) Zeta Potential Measurements

The zeta potential of fine solids suspended in a clarified separation water phase is plotted against more conventional measurements in distilled water shown in Figure 4-17. The bulk of the data lies above a 45^{o} line. An average line shows that the dispersed nature of the particles in the separation water phase is higher than that previously measured by using the conventional technique of suspended solids in distilled water.

Although the zeta potential of fine solids in the clarified separated water phase is probably a more scientific measurement, the trouble of obtaining the clarified water phase may preclude its measurement in favour of zeta potential measurements of a drop of water phase in distilled water, unless clarification of water phase sample is obtained for other more critical measurements.

Considering the details of the plot in Figure 4-17 it appears that 20 millivolts is a minimum value for the tar sands studies. This is about the threshold value (25mv) for flocculation. The tar sands with values of this order of magnitude *all* exhibit poorer processability. It was this type of observation, which suggested a correlation of zeta potential with processability.

(b) Relationships in Hot Water Separation

The zeta potential of finely divided solids suspended in the clarified water phase is plotted as a function of pH in Figure 4-18, essentially a minimum value of about 20 millivolts was obtained at pH's below 70. However, above 8 pH the zeta potential increased markedly. As this region also coincided with improved processability in terms of oil recovery and froth quality, zeta potential has been suggested as a correlating variable.

The zeta potential as a function of specific conductance from tar sand separation is plotted in Figure 4-19. The relationship is shown to be a function of the measurement technique, i.e. ZP_1 (in distilled water), ZP_2 (in the clarified water phase), and ZP_3 (in diluted clarified water phase

Figure 4-13

Relationship of Concentration of Sodium Salts and Specific Conductance of Solution

(See Table 42 for tabulated results on these specific salts, used in our studies)

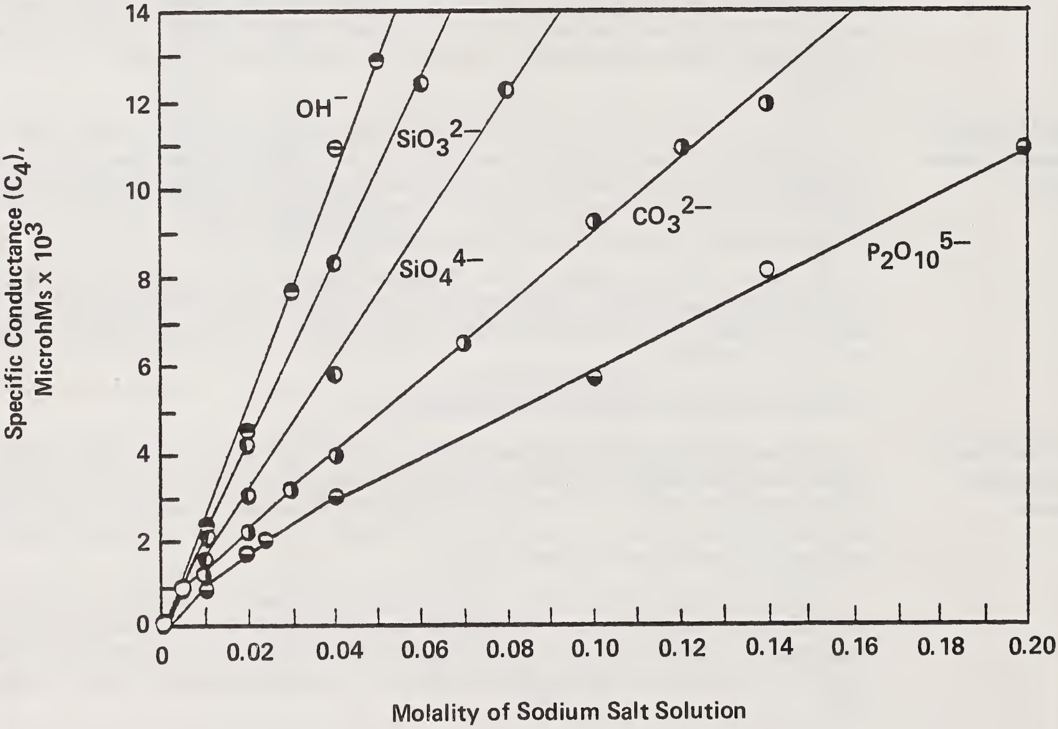


Figure 4-14

Relationship of pH and Specific Conductance for Fine Solids Suspensions in Different Sodium Salt Solutions

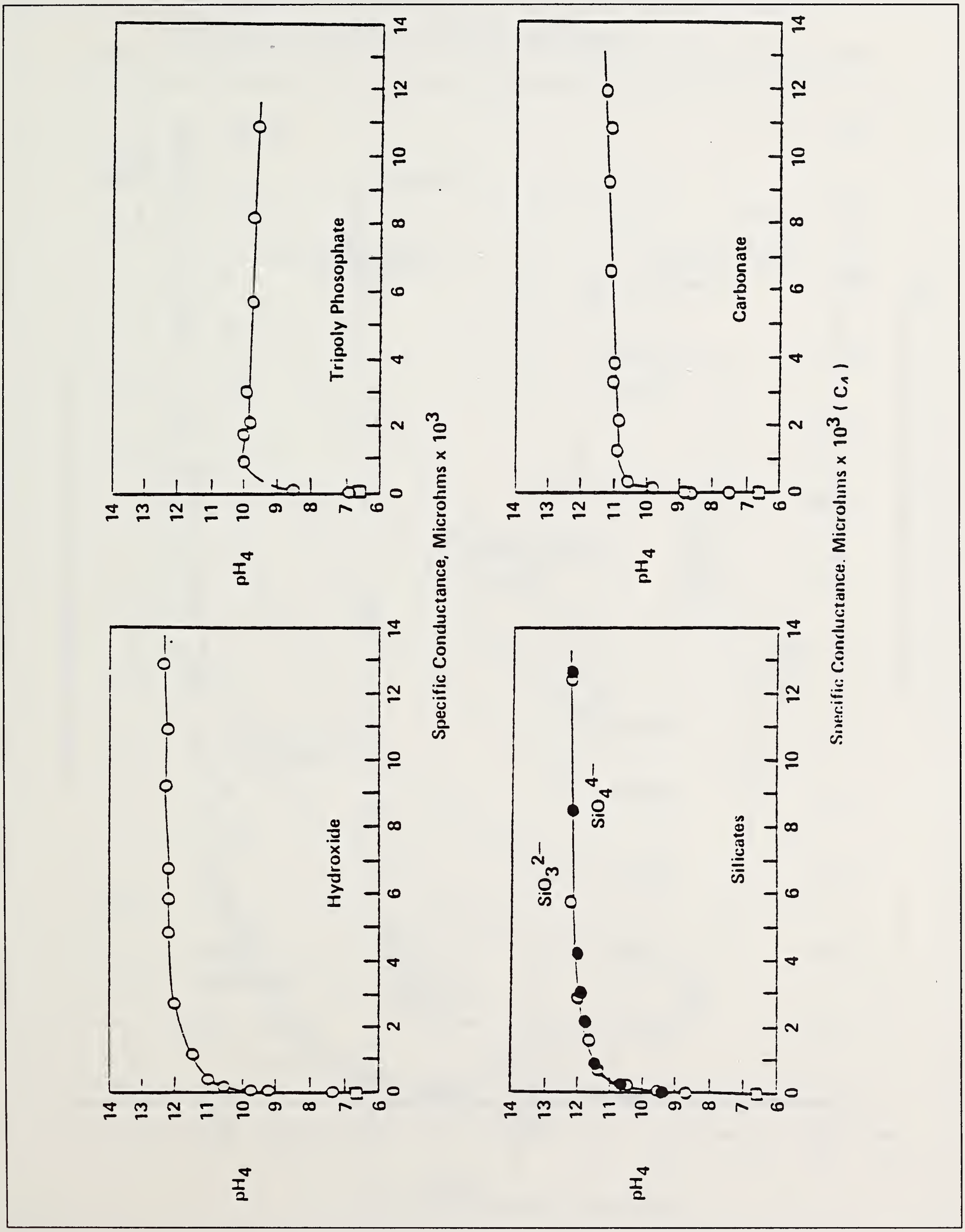


Figure 4-15

Sodium Salt Concentrations vs. pH of Solutions Used to Obtain Zeta Potential and Specific Conductance Measurements

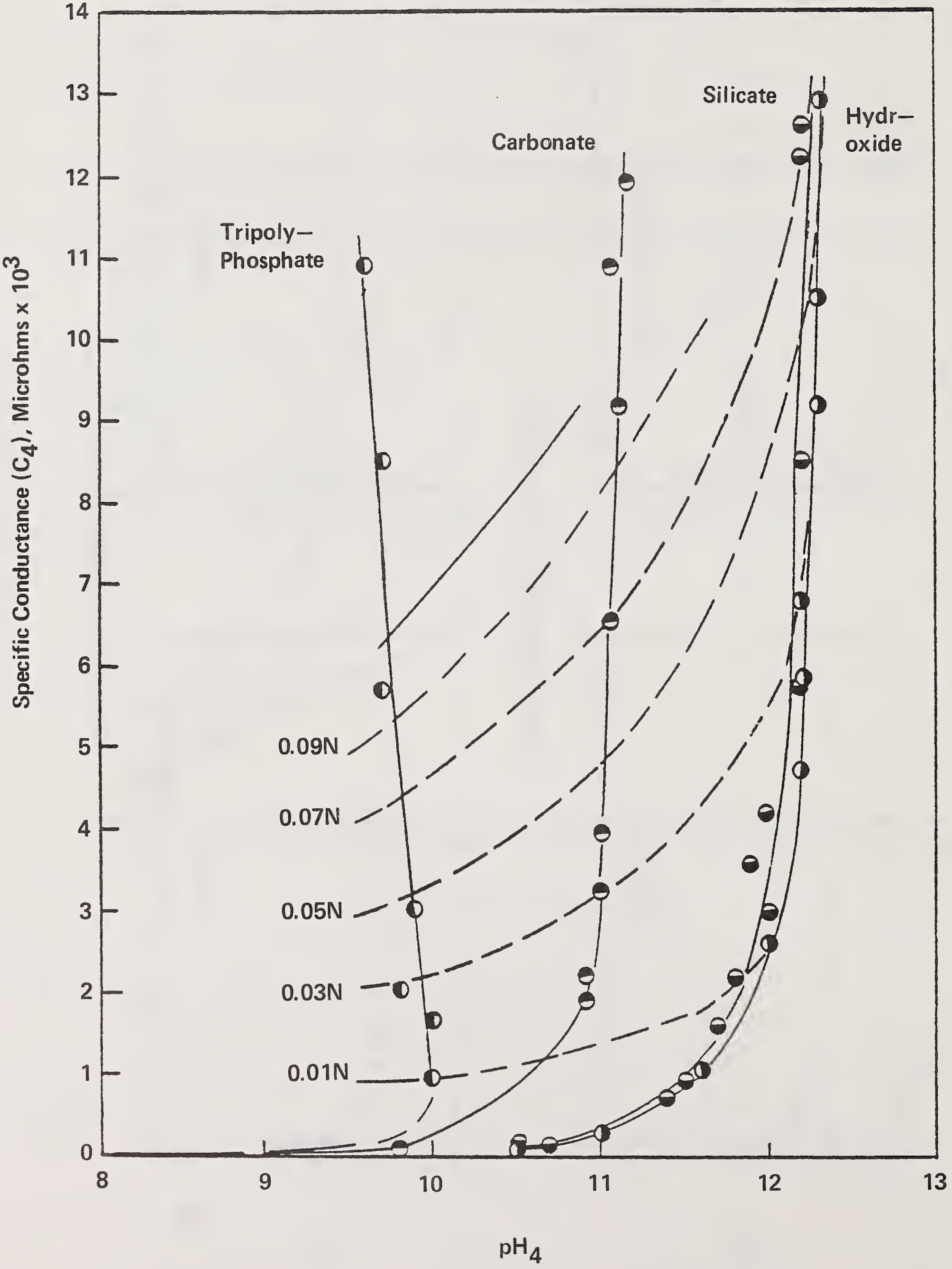


Figure 4-16

Specific Conductance and pH Relationship of Centrifuged Water Phase

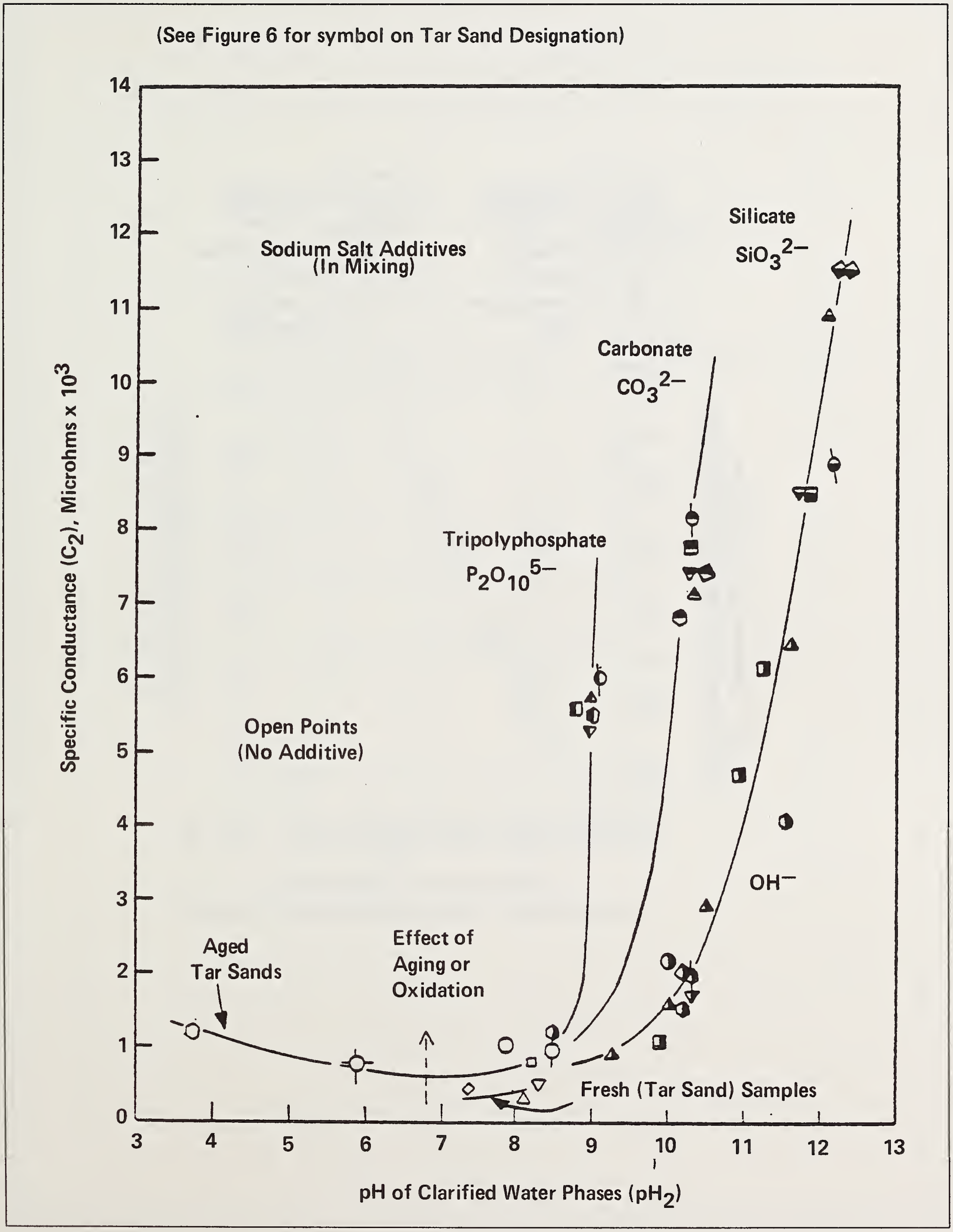


Figure 4-17

Relationship of Zeta Potential of Fine Solids in Different Water Phases

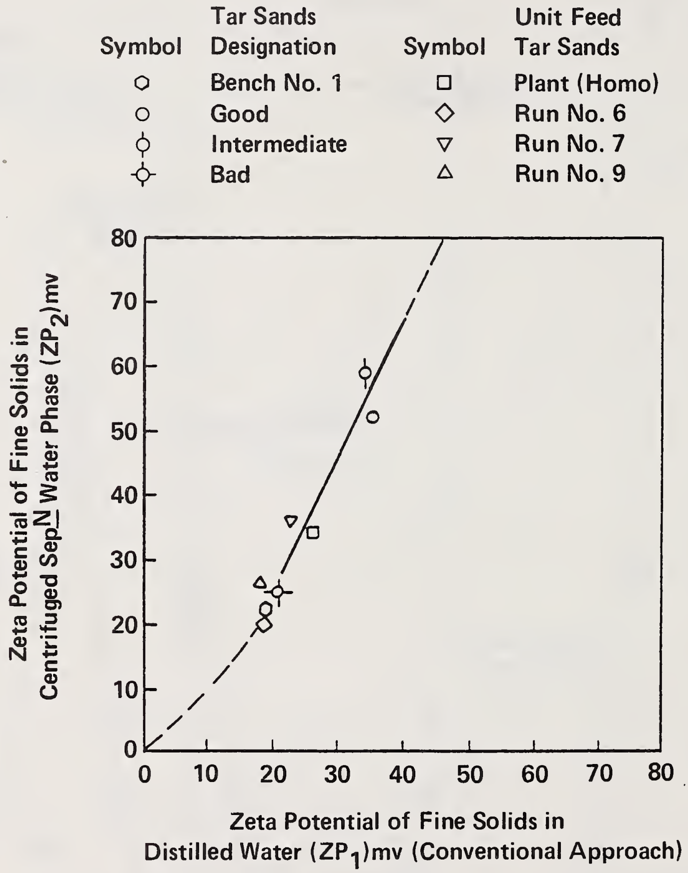


Figure 4-18

Relationship of pH and Zeta Potential of Various Beaver River Tar Sands

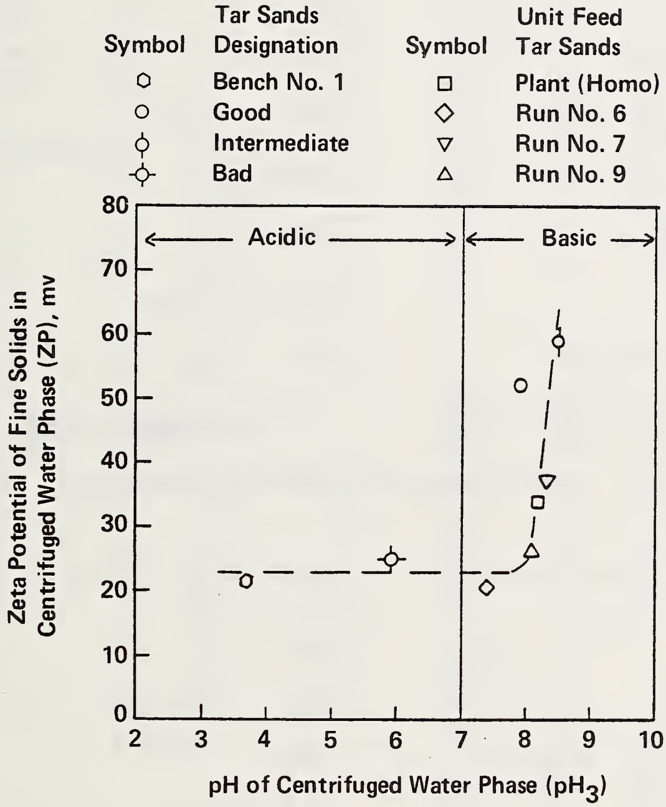
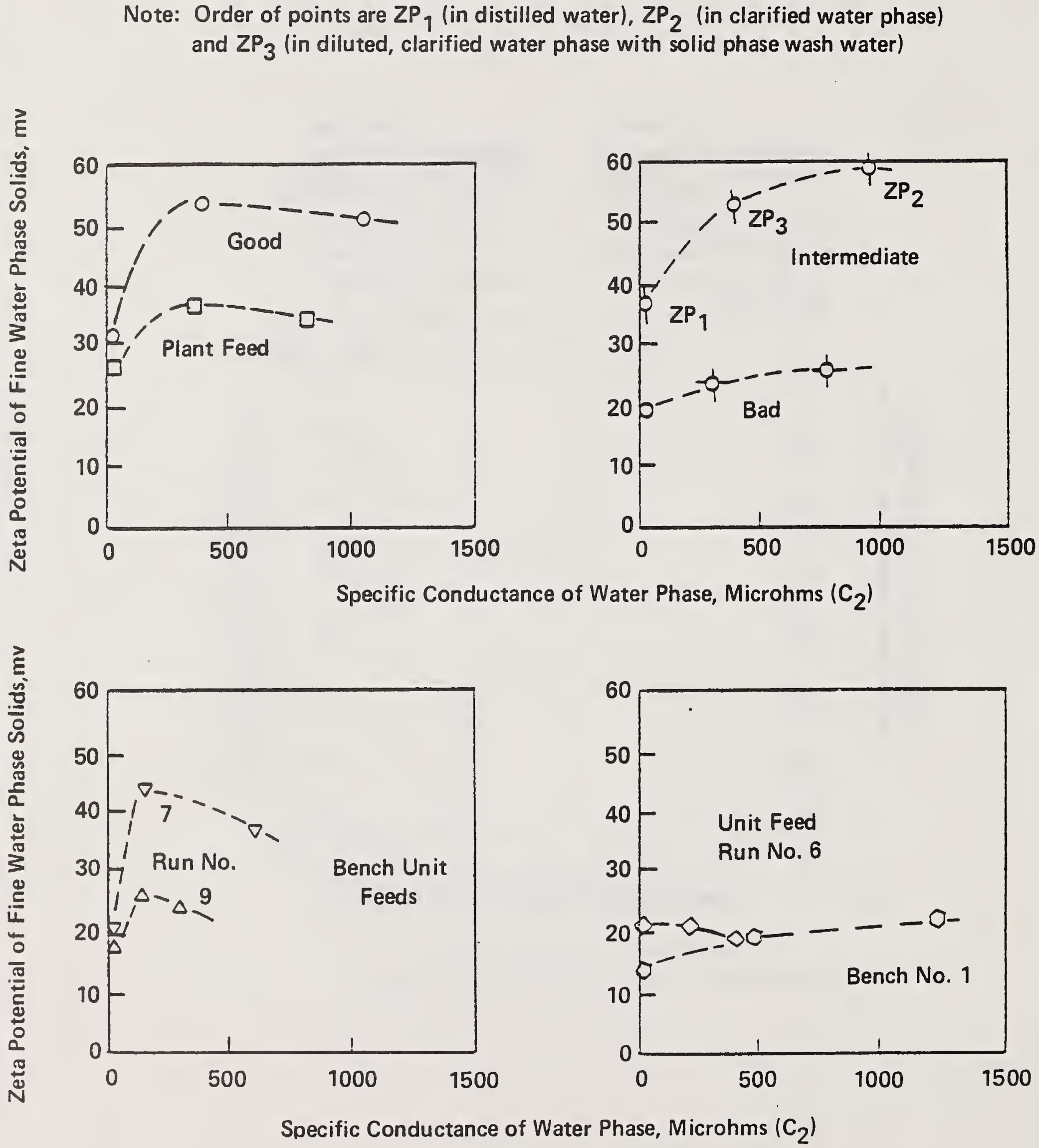


Figure 4-19

Zeta Potential as a Function of Specific Conductance of Water Phase



Note: Order of points are ZP_1 (in distilled water), ZP_2 (in clarified water phase) and ZP_3 (in diluted, clarified water phase with solid phase wash water)

Table 4-8

Measurements on Sodium Salt Solutions containing a drop of Water Phase from Hot Water separation of Bench Unit Feed-run No. 9 Tar Sand

Sodium Hydroxide			
Normality	**pH**	**S.C.**	**ZP**
Zero	6.4	4	22.1
0.00002	7.3	9	34.7
0.00006	9.2	18	32.9
0.0001	9.7	26	44.8
0.0002	10.5	88	37.2
0.001	11.0	306	44.5
0.004	11.6	1054	44.6
0.010	-	2312	40.9
0.011	12.0	2584	37.2
0.014	12.2	4760	39.1
0.024	12.2	5848	40.4
0.028	12.2	6766	38.9
0.030	-	7820	39.0
0.034	12.3	180	39.0
0.040	12.3	10880	31.7
0.050	12.3	12920	25.5
Sodium Tripolyphosphate			
0.00005	6.9	12	46.1
0.0001	8.5	43	52.9
0.010	-	850	55.7
0.012	10.0	950	51.3
0.020	10.0	1700	52.0
0.024	9.8	2006	52.8
0.04	9.9	2975	57.5
0.10	9.7	5700	53.4
0.14	9.7	8100	40.0
0.20	9.6	10880	34.1

Sodium Carbonate			
Normality	**pH**	**S.C.**	**ZP**
0.00005	7.5	10	35.9
0.0001	8.8	17	42.0
0.0002	9.8	58	38.8
0.002	10.5	299	55.1
0.01	10.9	1190	48.4
0.02	10.9	2210	45.7
0.03	11.0	3264	46.4
0.04	11.0	3944	48.0
0.07	11.1	6528	47.7
0.10	11.2	9180	49.1
0.12	11.1	10880	37.0
0.14	11.3	11900	28.4
Sodium Silicate (SiO_3^{2-})			
0.0001	9.6	27	39.1
0.0002	10.7	153	52.9
0.004	11.5	935	39.9
0.01	11.8	2159	41.3
0.014	11.9	3060	45.4
0.02	12.0	4233	47.2
0.04	12.2	8330	45.5
0.06	12.2	12410	34.6
(SiO_4^{4-})			
0.00005	8.7	11	36.8
0.0001	9.6	23	37.2
0.002	10.5	109	52.6
0.004	11.4	714	39.9
0.01	11.7	1632	43.4
0.02	12.0	2992	45.2
0.04	12.2	5814	39.4
0.08	12.2	12240	30.7

Figure 4-20

Relationship of Zeta Potential of Fine Solids in Different Water Phases

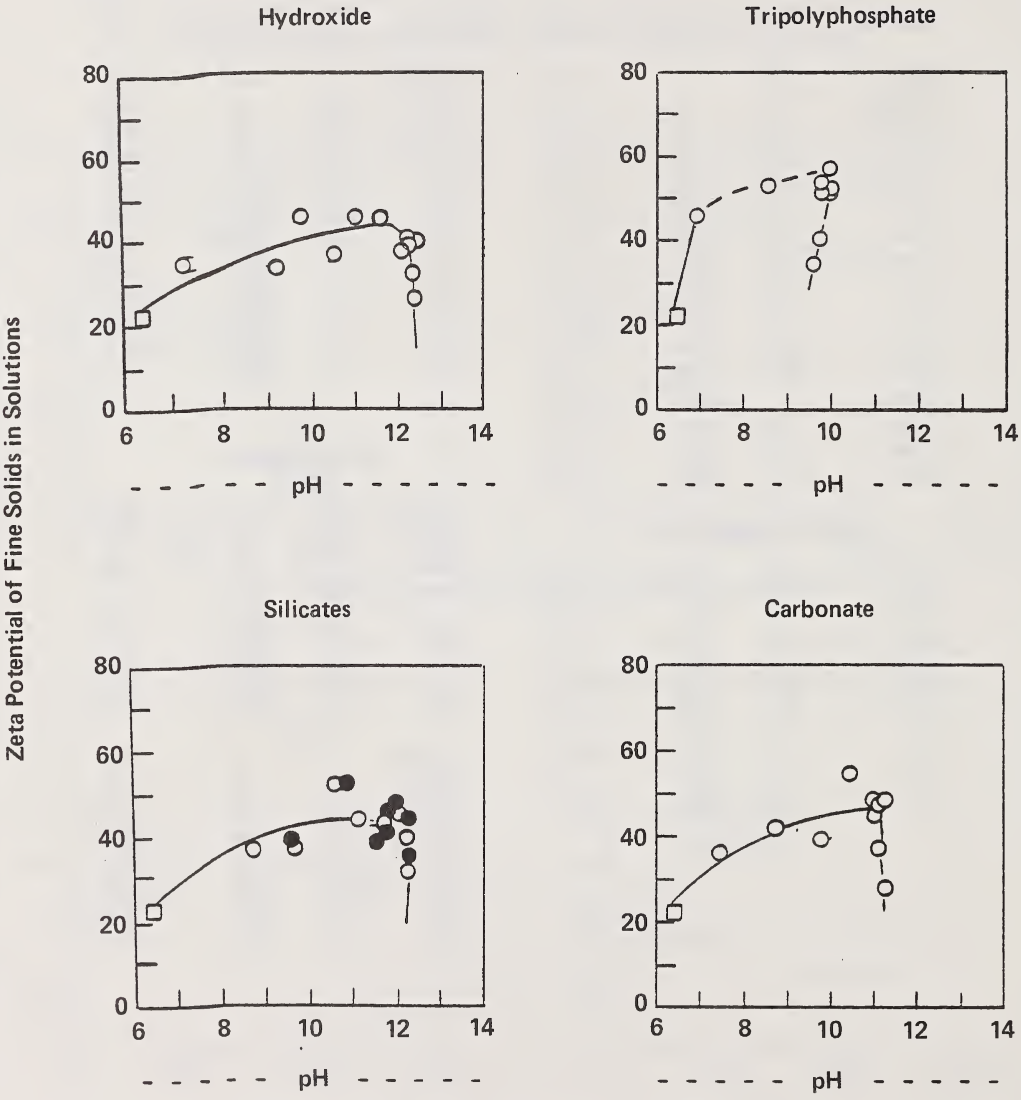


Figure 4-21

Relationship of pH and Zeta Potential of Fine Solid Suspensions in Different Sodium Salt Solutions

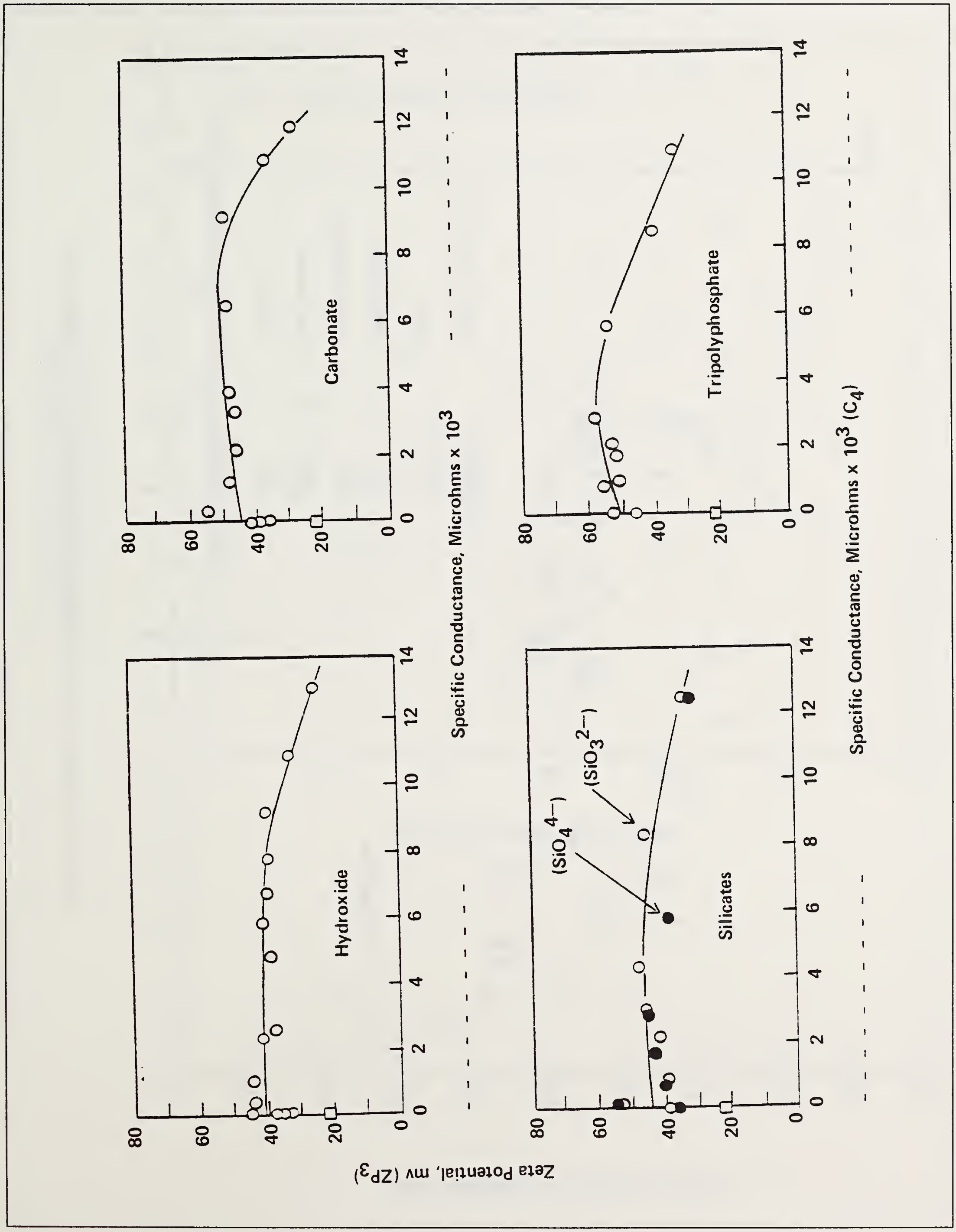


Figure 4-22

Specific Conductance and Zeta Potential Relationship of Centrifuged Water Phase

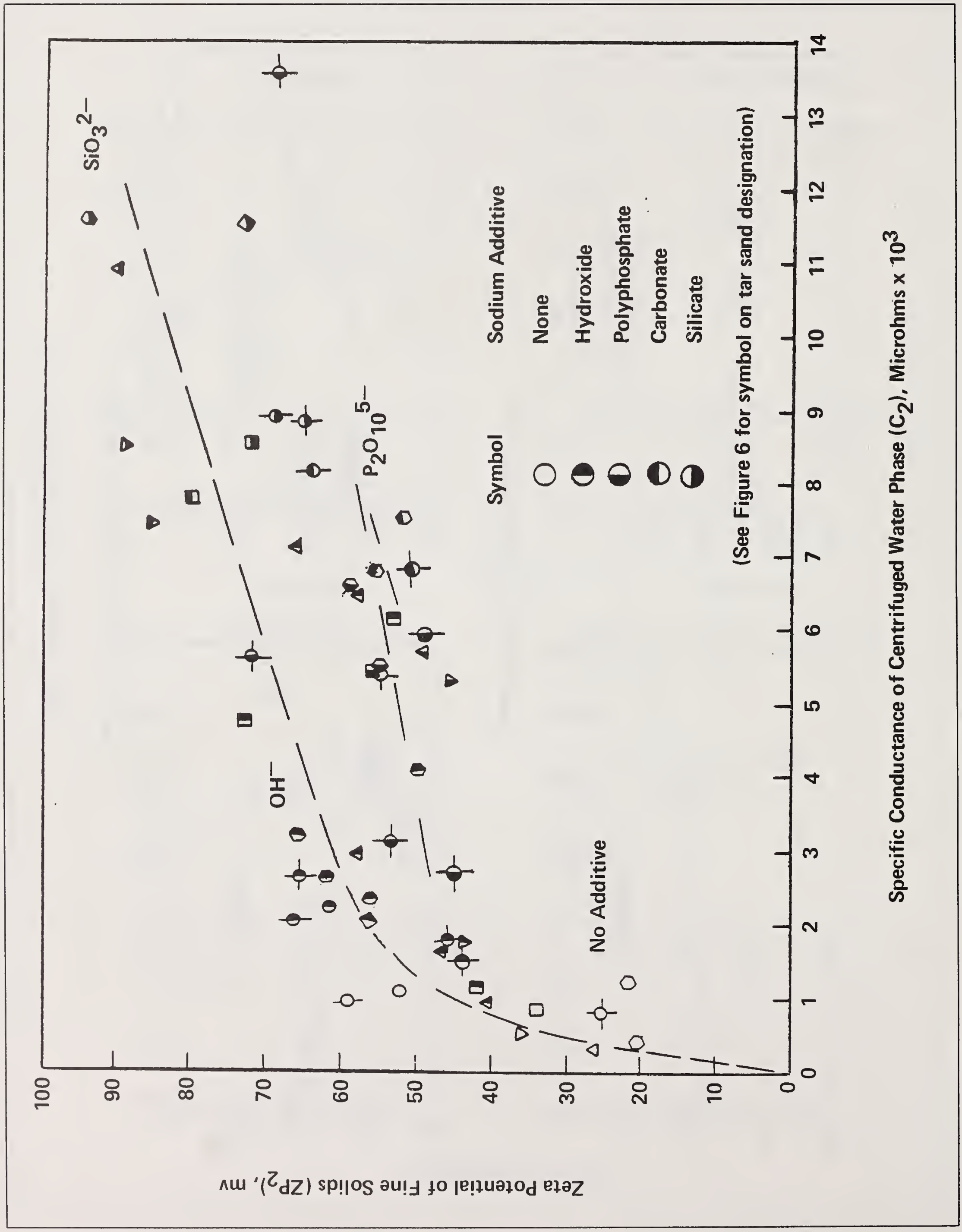


Figure 4-23

pH and Zeta Potential (ZP2) Relationship

Note: Points are derived using Figure 6

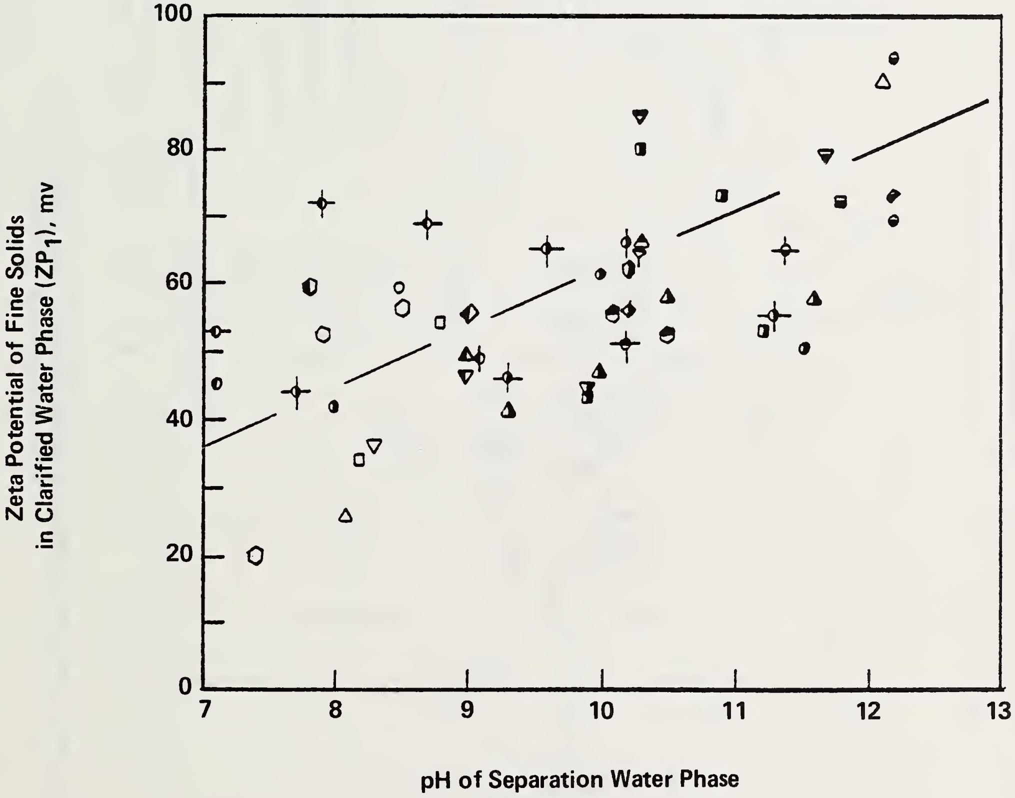


Figure 4-24

Specific Conductance and Zeta Potential Relationship

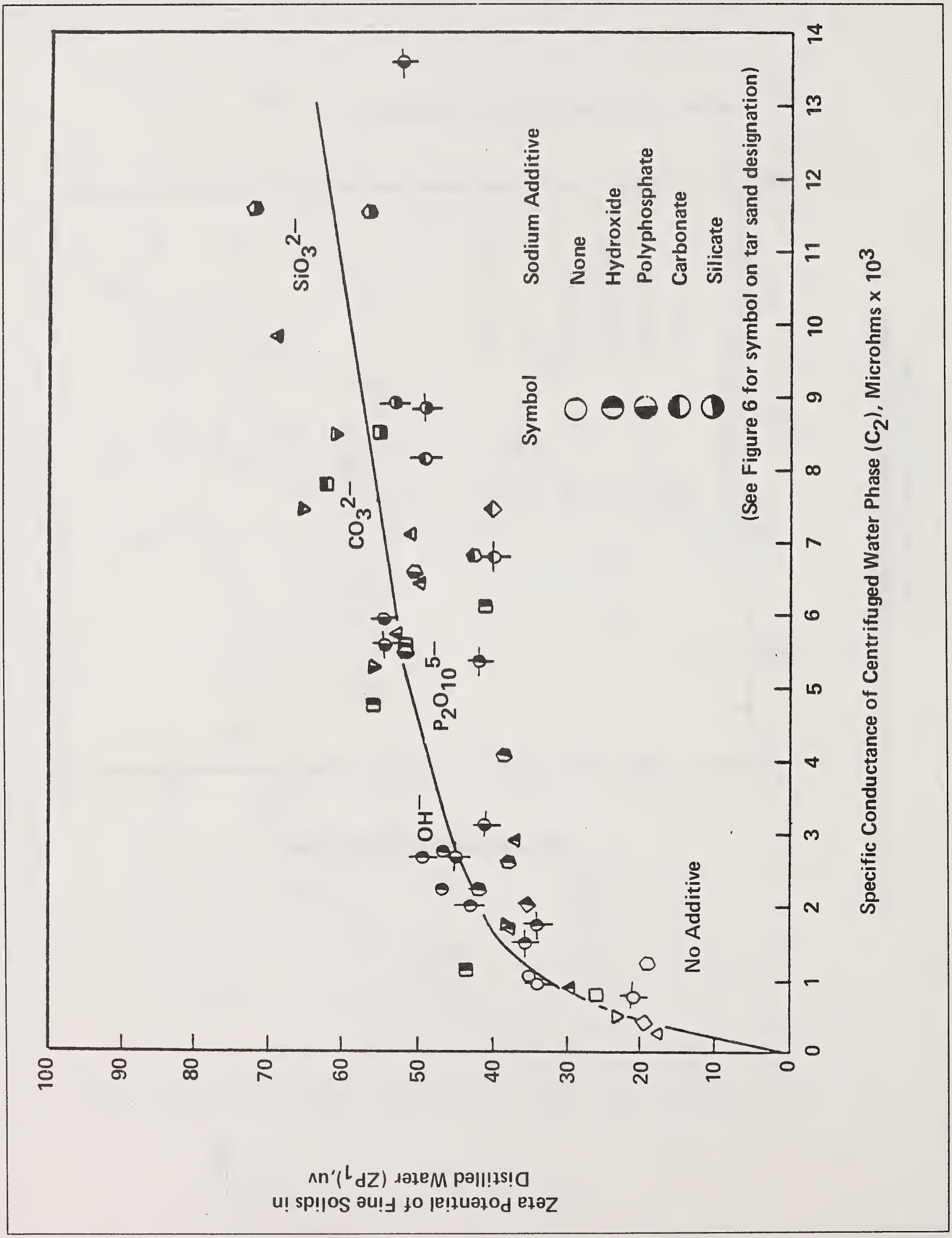
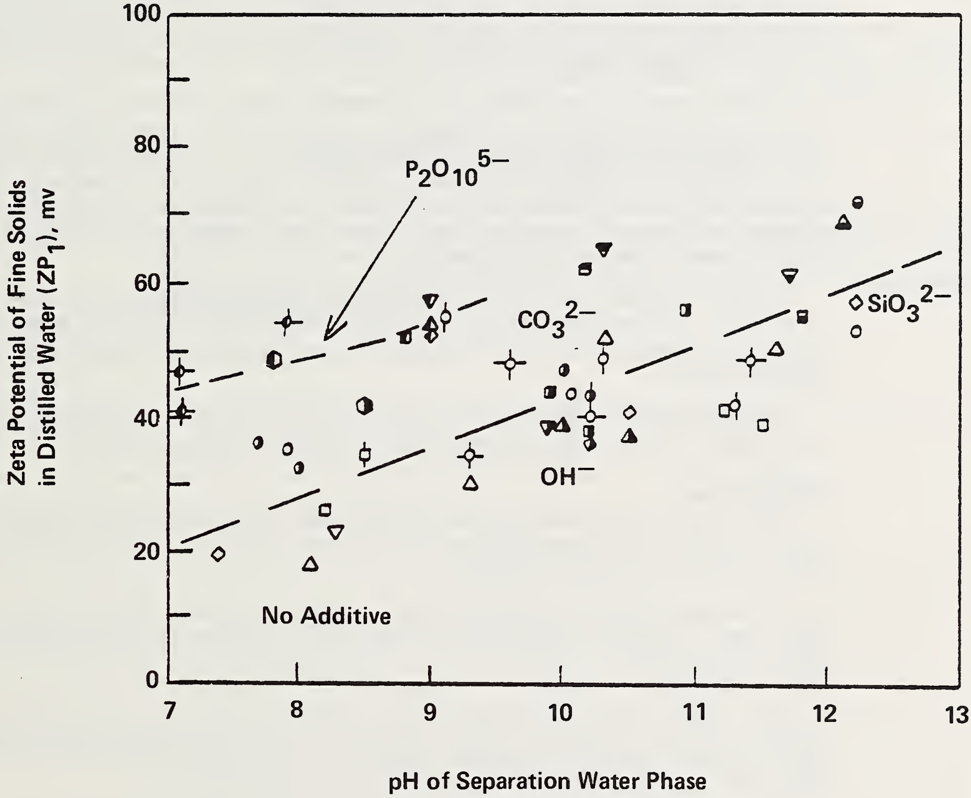


Figure 4-25

pH and Zeta Potential (ZP_1) Relationship



with solid phase wash water). This shows that zeta potential and specific conductance are not interrelated simply with dilution.

(c) Relationships with Addition of Chemicals

The relationship of zeta potential of a drop of fine solids in solution of different sodium salts as a function of pH is shown in Figure 4-20. No simple relationship is apparent between these variables.

The relationship of zeta potential of fine solids suspended in solutions of different sodium salts as a function of specific conductance is shown in Figure 4-21. No significant relationship is apparent. The scatter of the data at low specific conductances might be associated with changes in the structure of the solid double layer due to changes in counterion concentration in solution, which may contribute to the difficulty in accurate measurement of zeta potential in this area.

The zeta potential of fine solids as a function of the specific conductances in the clarified water phase (see Appendix for technique) from separation studies is shown in Figure 4-22. In spite of the scatter in the data there is an indication that different curves for different anions of the sodium additives may occur. These curves appear to be approximately an inverse plot similar to Figure 4-20, for specific conductance versus pH. A general relationship between pH and zeta potential should therefore exist, and is show in Figure 4-23. A wide scatter in the data is evident using this method of zeta potential measurement.

A simpler correlation was obtained between zeta potential of fine solids in distilled water and specific conductance of the clarified water phase, Figure 4-24. The relation of this type of zeta potential measurement with pH of separation is shown in Figure 4-25. Again a simpler correlation is obtained.

The supposition that zeta potential measurements of fine solids in the clarified separation water phase is a more precise correlating variable in separation is not substantiated.

4-3-3 Summary

The pH of the water phase from Hot Water Flotation is quite characteristic of the specific type of tar sand fed to the separation process. This parameter can be accurately measured, and its relationship with processability is known.

pH has been found to be independent of the specific conductance (ionic strength) of the water phase. It, therefore, represents only a critical condition of separation, which is not affected by the amounts of salt in solution. However, it is significantly affected by the types of anions added in separation.

Zeta potential in general terms of flocculation-dispersion at about 25 mv does appear to be related to tar sand processability. Further, zeta potential is correlated simply with pH. However, this correlation is not precise or sensitive enough to recommend zeta potential, based on these studies, as a critical parameter in the control of a commercial operation.

Inter-relationship of pH of separation with zeta potential of fine solids and specific conductance (ionic strength) of the water phase have been established. However, these are far from precise, and are affected by the types of sodium salt additives used in separation. Applications of these measurements as paramters of pH in control of a commerical plant does not appear promising.

The high zeta potential of the suspended clay and sludge (clay/oil) result in very stable suspensions. Using zeta potential reduction techniques by chemical addition in other studies have demonstrated complete clarification of water phases. However, this approach is not economic.

- *As the above discussion of water phase properties has emphasized the inorganic contribution, the small but significant contribution from aqueous soluble oil should also be included. Some of the more relevant findings are summarized below:*
- *Aqueous soluble oil components have been found in all systems of oil in contact with an aqueous phase, e.g., the water phase from hot water flotation separation.*

- *The solubility of the polar hydrocarbons in aqueous media have been found to increase (a) with increasing temperature, (b) with increasing amounts of highly polar hydrocarbons in the oil, and (c) markedly at high and at low pHs.*
- *The fluorescence of soluble acid-oil components generated in alkaline solutions is essentially constant with decreasing pH. Fluorescence of the soluble base-oil component in acidic media decreases with increasing pH. This indicates the presence of two entirely different soluble oil components.*
- *The soluble oil also changes the pH of the contacting solution. The net effect is that the oil behaves as an amphoretic, i.e., an acid in alkaline media and a base in acid solution.*
- *These two main types of naturally occuring polar hydrocarbons have been isolated. The base soluble oil component appears to be primarily a carboxylic acid. The acid soluble oil component is probably a nitrogen heterocyclic with other functional groupings containing sulphur e.g., porphyrin or resinous acid.*
- *Thus, the addition of pH controllers are affected by the solubility of the oil (vice versa) as well as being adsorbed by clay minerals.*

Significant amounts of Na, K, Cu, Fe, Cl, CO_3, or HCO_3, SO_4 silicate ions have been readily separated from tar sand slurried with water. The amount of ions separated vary widely with different tar sands, and is estimated to be ~0.5 wt %. These ion types and amounts however change with exposure to air (oxidation) and with chemical conditioning with caustic solutions in hot water separation of oil sands.

5

GAS

The presence of gas in the oil sand structure can be readily demonstrated by evacuating a flask containing small lumps of fresh oil sands. Bubbles appear at the surface on reducing the pressure. This is more dramatic when conducted under water. The first bubbles that appear are uncontaminated with oil. However, as more gas is lost from the structure, the bubbles appear at the surface of the oil sands covered with a thin film of oil, which is carried to the water surface. Clean sand is observed to break from the lumps and accumulate at the bottom of the flask. If the pressure is reduced initially to a low value, e.g. less than 100 millimeters of mercury at room temperature, the evolution of gas from the lumps of oil sands is very rapid and the lumps float. On breaking the vacuum, however, the evolution of gas ceases and the lumps sink to the bottom of the flask. If the tar sands are pre-mixed with water and then subjected to a vacuum, particles of oil can be observed to float to the surface by virtue of "dissolved" gas bubbles, which are held at the surface of these oil particles by a thin oil film. On breaking the vacuum, these bubbles collapse and the oil particles sink. The process can be repeated by further evacuation. Thus the movement of these oil particles can be controlled by the pressure which can be used in separation.

Experiments carried out in which tar sand in one container was flushed with helium and then connected to a large evacuated vessel. The gas released was collected in the vessel, removed by water displacement and analyzed. This operation was repeated on the same tar sand sample. The results indicated the gas to be a mixture of N_2, CO_2 and methane with very small quantities of higher molecular weight hydrocarbon, particularly propane. Gas samples collected from atmospheric distillation of crude have confirmed the existence of these hydrocarbons as well as hydrogen. However, this latter component, e.g. 12 mole% vs 23 mole% for methane, may have resulted from dehydrogenation of naphthenes at the temperature needed to cut a 650°F final cut point.

Hence, the amount of gas in the oil sands is small but can be significant in separation. Part of the gas appears to be "free" in the voids that is presumed to be predominantly CO_2 (and N_2), which is also a major component of the gas exiting from fresh core holes. Gas associated with oil separation appears to be predominantly methane.

The source of CO_2 was thought to be carbonates, such as siderite, calcite, etc. The presence of nitrogen was attributed to air trapped in the original formation, and the absence of oxygen attributed to reaction with either mineral or oil.

II. BEHAVIOUR

6

FLOTATION

The technique of separating oil sands by hot water flotation at about 180°F was first pioneered by Dr. K.A. Clark about forty years ago. Studies of the process were on a large pilot plant scale and concerned with proving the technology and overcoming the many materials handling problems. Although these studies provide a general definition of the process and its practicability, as well as its associated problems, little clear cut data on the interaction of process variables are available.

In order to measure the operative factors and to understand the principles in hot water flotation that might be applied in larger scale developments, simple laboratory tests were developed to obtain comparative data.

A beaker technique (100g) was originally developed at Sarnia, to obtain a measure of the processability of tar sands in Hot Water Flotation separation for comparison with the Sand Reduction Process. Results obtained without aeration were compared with Clark's original pilot plant data, and with aeration were compared with C.S.A.'s Mildred Lake Bench Unit data. Good agreements based on oil recoveries were obtained by suitably adjusting the conditions of separation. The results of these original studies are discussed in Section A and are mainly concerned with the oil sand state, sampling, and handling. Control of process variables was not precise enough, and reproducibility to some extent varied as a function of the operator. However, the technique was adequate for comparative exploratory research and preliminary evaluations of process variables.

A modification of the technique developed at Sarnia used a semi-mechanized Brass Pot to obtain better process variable control and reproducibilities than was achieved in early beaker studies. This approach substantially improved reproducibility between different operators. The design basis of the separation technique was to simulate oil recoveries obtained in the Mildred Lake Bench Unit. This separation technique was mainly directed at maintaining an overall low energy input process. The results obtained using this method of separation as a research tool to investigate process variables are discussed in Section B. Standard conditions are not necessarily optimum for different tar sands.

A further modified Pot procedure using standardized conditions to simulate pilot unit operations was adopted and used to demonstrate process control of the more critical process parameters in hot water flotation as described in Section C.

Some detailed data that support the findings discussed in the text is included in the Appendix.

A. Original Beaker Experiments

A beaker technique was originally developed at Sarnia to obtain a measure of the processability of tar sands in hot water flotation for comparison with the Sand Reduction Process that will be discussed in Section 9. A need for a laboratory extraction technique to quickly evaluate the processability of different tar sands, prompted the adoption of this test. Control of process variables was not precise, but adequate for comparative work. However, this technique proved to be a very useful research tool in obtaining some preliminary data on the variability in processing different tar sands, and the effect of process variables. (See Appendix V6).

This section has been included to preserve the original concepts and interpretation, which were made at the time and published in memoranda on completion of the work. The concepts and the inferences of these studies were substantiated and developed further by subsequent work using more mechanized and reproducible procedures.

6-1 Effects of Fines Without Aeration

As fines containing clay minerals appeared to be deleterious to high oil recovery in hot water flotation, the effect of adding fines from large "clay" lenses taken from the formation was investigated. A good quality Area B tar sands was used as a feed. One set of results in Table 6-1 are compared with those found earlier by K.A. Clark in the original pilot plant development of the hot water separation process, at Bitumount, Figure 6-1. There is good agreement between the two sets of data. These data show that without aeration there is a loss of oil from froth to sludge (middlings today) as the amount of clay in the feed increases. The composition of the froths from these experiments also deteriorate with clay addition, see Table 6-1. The solids content of this froth increased substantially with increasing fines in the tar sand feed fines.

6-2 Comparison with Pilot

A comparison of the results obtained in the CSAI's Bench Unit using an air stripping separator, and the laboratory extraction method with secondary aeration, on Area "B" good quality tar sand is shown in Table 6-2.

It will be noted that both in the Bench Unit operations and the laboratory extractions, similar froth quality and oil recoveries were obtained. Small lumps of what appeared to be "oil-wet-sand" were obtained in the separated sand. These were presumably "dried" tar sand particles resulting from surface exposure to the atmosphere or formed during blasting in this area. This factor could cause variation in the oil recoveries from the laboratory tests, due to the small sample size used as well as aging through evaporation and oxidation.

A similar comparison with a medium to poor quality tar sand is shown in Table 6-3. In general, fair agreements in both froth qualities and oil recoveries were obtained. The oil recoveries from the tar sands used in the first two shifts are approximately the same for both the Bench Unit and the laboratory extractions. Further, the oil recoveries from both extractions increased in the third shift, indicating a change in feed quality; however, the higher oil recovery in the Bench Unit for shift B2 was achieved by producing more froth of the same quality than in previous shift operations. In the laboratory, the increased oil recovery in Run #9 was obtained by producing more froth of a better quality. The inconsistency in this part of the data comparison could be due to an error in one of the many different operations by which these results were obtained, e.g. tar sand sampling, and homogenization, product sampling, analyses and methods of data computation.

Table 6-1

Effect of Clay in Hot Water Separation (Initial Beaker Experiments)

(Tar Sand Contained 14 Wt% Oil, 6 Wt% Water, 78 Wt% Sand and 2 Wt% Clay)

Experiment Number	**10**	**9**	**8**
Conditions			
Additions in Mixing, Wt%(2)			
Clay(3)	-	8.6	43.0
Water	10		
Steam	Yes		
Temperature, °F	180-190		
Type of Mixing	Mild (Beaker and Spatula)		
Premixing Time, min	2		
Aeration	No		
Sand Washing	Yes		
Results, Wt%			
Material Recovery	95.0	96.5	97.0
Yield of Oil Froth	13.3	12.3	11.9
Sludge	6.4	16.4	47.2
Sand	80.3	79.9	83.9
Composition of Oil Froth			
Water	37.0	36.7	37.2
Solids(1)	4.0	5.5	29.6
Oil	59.0	57.8	33.2
Oil Content of			
Sludge(1)	43.6	18.7	57.3
Sand(1)	0.26	0.46	1.07
Oil Recovery in			
Froth	80.3	69.6	39.3
Sludge	18.4	28.4	56.2
Sand	1.3	2.0	4.5

(1) Based on Ash Determinations
(2) Wt% on Tar Sand
(3) Oven Dried Basis

Figure 6-1

Effect of Clay on Oil Recovery in Hot Water Process (Initial Beaker Experiments)

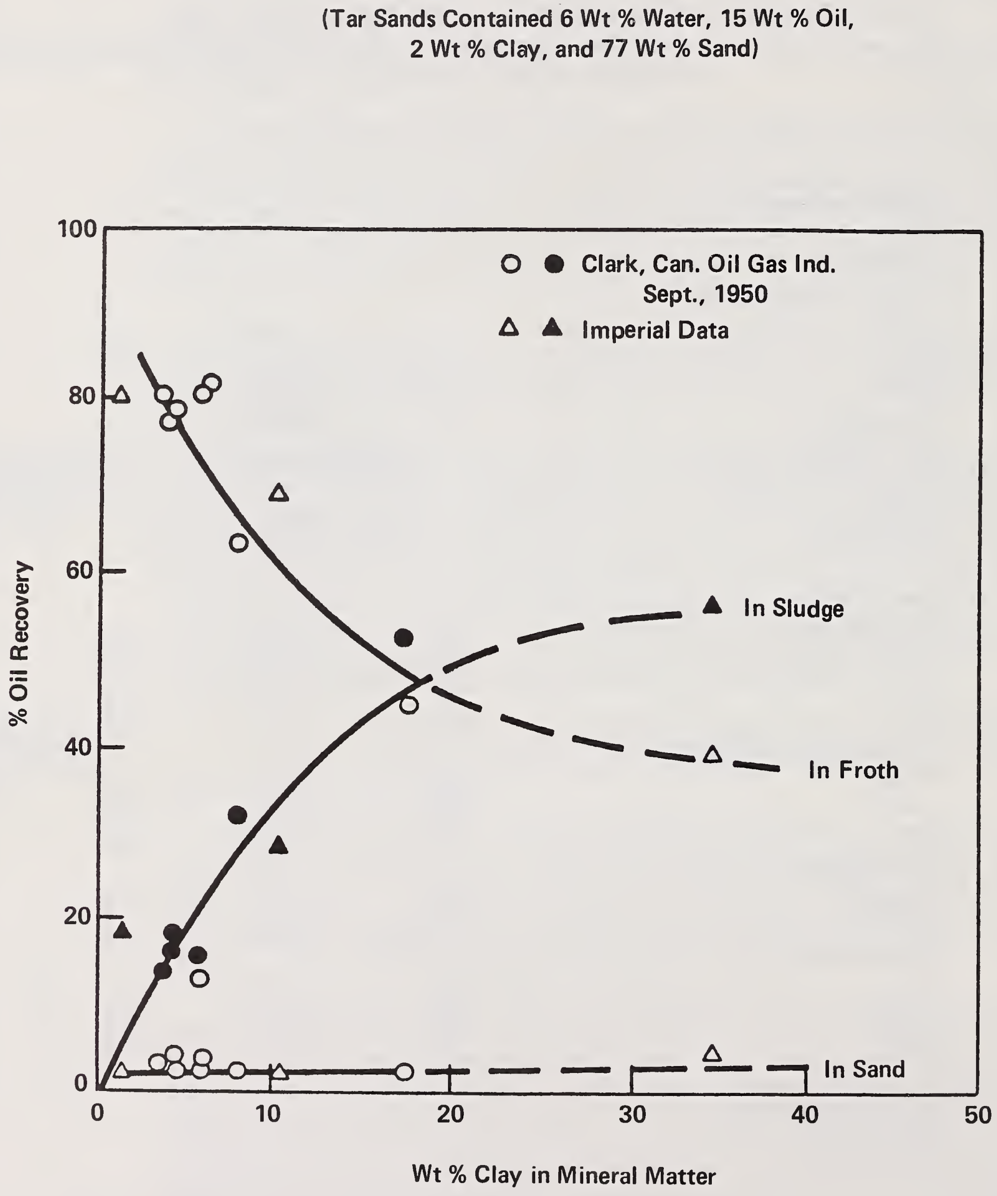


Table 6-2

A Comparison of Tar Sand Separations in the CSAI Bench Unit and Imperial's Laboratory Technique (Good Quality Tar Sand - Area "B")(4)

Operation	CSAI Bench Unit(5)			Sarnia Extraction		
Run #2, Shift (Expt No.)	B_2	C_1	C_2	(#1)	(#2)	(#6)
of April 1962	11-12th			(12th)	(13th)	(14th)
Hours of Sampling (April 11-12th)	1400/1800	1800/2200	2200/0200	1430(1)		
Feed R_8	1500 lb/hr			100g		
Tumbler (Mixing) Water, %(2)	19	21	20	27		
Flooding Water, %(2)	21			50		
Stripping Water, %(2)	21			--	--	--
Air Rate, SCF/hr/lb Tar Sand	0.24			0.24		
Froth Composition, Wt%						
Water	27.6	27.4	29.6	31.0	31.2	30.8
Solids	13.0	12.9	13.3	13.5	12.4	11.4
Oil	59.4	59.7	57.1	55.5	56.4	57.8
Yields, Wt% (Water Free Basis)						
Froth	-	-	-	15.8	14.2	15.6
Sludge	-	-	-	6.2	6.4	7.7
Sand	-	-	-	78.0	79.4	76.7
Material Recovery, Wt% (Water Free Basis)	-	-	-	99.0	99.0	101.0
Oil Recovery, Wt% In (Output)						
Froth	>95			95.3	97.3	86.7
Sludge	-	-	-	2.6	2.3	8.8
Sand	-	-	-	2.1(3)	0.4	4.6(3)

(1) Spot sample taken from Bench Unit Feed

(2) Weight percent water content or addition on Tar Sand

(3) Small lumps of "Oil wet sand" can be seen in the separated sand from both the laboratory experiments and from the Bench Unit, that are not separated by hot water

(4) See Table 1 - for Tar Sand Analyses

(5) Data obtained from CSAI Technical Group. Stream analyses obtained by CSAI Analytical Laboratory. Stripper used for flotation.

While no attempt was made to optimize the laboratory test for simulating the Bench Unit operations, the results showed a remarkably good agreement, Table 6-2 and 6-3. The difference in behaviour patterns of the two tar sand qualities are clearly shown in both the Bench Unit and the laboratory studies.

This success in being able to simulate processability of larger pilot operations in the laboratory test now became the means to be able to investigate the water flotation process in greater depth.

(a) Tumbler Tests

The laboratory separation technique was also adapted to evaluate two effluent from the Bench Unit tumbler test program. The results are shown in Table 6-4. It will be seen that there is a difference in froth compositions and yields. These differences may reflect more the variability of tar sand feed quality rather than change in process variables. This is indicated by the different calculated oil contents of the tar sand feeds to these tests.

6-3 Variability of Oil Sands

The processability of a number of core samples was evaluated. The results of one example are summarized in Table 6-5. Inspection of the data shows a wide variation in processability with increasing oil sand grade that appears to increase, Figure 6-2.

The wide variability of tar sand quality is also illustrated by the data from the area of Auger Hole 9, Area D, Table 6-5. The processability of these samples is compared with that of a sample from Area B. It will be noted that similar results were obtained with the Area B sample in experiment 1 and with the Area D sample in experiment 2. In fact, a slightly better separation was obtained with this Area D sample taken approximately 14 ft north-east of Augher Hole 9 x 2 at a depth of 5-10 feet, than with this particular Area B sample. The separated sand from experiment 2 was very clean and all passed through a 40 mesh U.S. Sieve. However, a sample taken at the same depth and about 10 ft east of the same Auger hole, exhibited a poor processability with an oil recovery in the froth of only 85%, (experiment 3). It is interesting that the solids content of the froth obtained from this sample is low.

Another example of a low solids content froth was observed with a sample taken only about 5 ft east of Auger Hole 9 x 2, (experiment 8). With this tar sand sample, however, a high oil recovery was obtained. Experiments 4 and 5 with lower oil content, tar sands gave poor results. A hand dug sample from Auger Hole 9 x 1, (experiment 6) and another sample received at Sarnia described simply as Hole 9, Area D, (experiment 7) both gave poorer oil recoveries than experiments 4 and 5, although these samples had higher oil contents.

There does not appear to be any consistent pattern in this data, with the generalized exception that higher oil recoveries are obtained with tar sands high in oil content, Figure 6-1. However, it is shown clearly that a particular sample of tar sands taken from Location D could exhibit any oil recovery. The wide variation in processability is not only paralleled by a wide variation in composition, but there are presumably other factors influencing the separation, such as exposure leading to tar sand composition changes from water loss and oxidation. The non-homogeneity of the tar sands can also be observed from freshly cut faces in the formation. Within a few inches vertically in the face, thin grey and red clay bands, low and high oil content tar sands, clean sand and small "oozings" of oil can be seen. However, the feed from large scale mining operations might be expected to be much more uniform in composition and processability.

This non-homogeneous composition of tar sands requires that larger representative quantities from a given location be homogenized before samples are taken for small scale laboratory work. Homogenizing fresh tar sand samples has been found to have little or no significant effect on processability results.

6-4 Effect of Auguring

The comparison of augured and hand dug samples from Holes 9 x 1 and 9 x 2 is shown in Table 6-7. The froth composition, yields and oil recoveries are of the same order of magnitude by oil recoveries are low presumably due to aging. The exception is a high solids content of the froth from the hand dug samples.

Table 6-3

A Comparison of Tar Sand Separations in the CSAI Bench Unit and Imperial's Laboratory Technique (Medium to Poor Quality Tar Sand - Location "D"- Area of #9 Auger Hole)

Operation	CSAI Bench Unit(5)			Imperial Extraction			
Run 5 Shift (Expt No.) of April 14, 1962	A_1	A_2	B_2	(#7)	(#8)	(#9)(4)	(#5)
Hours of Sampling (April 14, 1962)	24.30/0330	0330/0.630	1000/1300	2430/0330	0330/063	1000/1300	0845(1)
Feed	500 lb/hr			100g			
Tumbler (Mixing) Water, %(2)	30		32	26			
Flooding Water, %(2)	14		8	50			
Stripping Water, %(2)	28		8	-	-	-	-
Air Rate, SCF/hr/lb Tar Sands	-0.72		-	0.24			0
Froth Composition, Wt %							
Water	43.0	44.3	43.5	38.1	40.4	28.8	32.8
Solids	9.1	9.7	9.5	13.4	12.4	7.5	5.8
Oil	47.9	46.0	47.0	48.5	47.2	63.7	61.4
Yields, Wt % (Water Free Basis)							
Froth	6.6	5.8	9.6	6.2	5.6	9.7	5.3
Sludge	-	-	-	16.0	16.3	11.5	21.2
Sand	-	-	-	77.8	78.1	78.8	73.5
Material Recovery, Wt % (Water Free Basis)	-	-	-	98.3	99.0	100.1	95.6
Oil Recovery, Wt % In (Output)							
Froth	60.8	58.7	73.7	55.7	56.2	68.6(3)	51.4
Sludge	39.2	41.3	26.3	33.9	39.0	23.8	39.4
Sand	39.2	41.3	26.3	10.4	4.8	7.6	9.2

(1) Spot sample taken from Bench Unit Feed

(2) Weight percent water content or addition on Tar Sand

(3) The tar sand sample taken and used in this experiment behaved like that of better quality (i.e. higher) oil content than other samples tested

(4) See Table 1 for Tar Sand Analysis

(5) Data obtained from CSAI Technical Group. Stream analyses obtained by CSAI Analytical Laboratory. Stripper used for flotation.

Table 6-4

Laboratory Extraction Technique Can Be Adapted to Study Process Variables in the Bench Unit such as Evaluation of Tumbler Effluent

Separation Test	**Sarnia Beaker**	**CSAI Tumbler**
Water in Slurry(1)	20.7	24.2
Froth Composition, Wt%		
Water	36.1	30.0
Solids	6.9	5.2
Oil	57.0	64.8
Yields, Wt% (Water Free Basis)		
Froth	8.9	11.1
Sludge	11.2	8.0
Sand	79.9	81.0
Oil Recovery, Wt% In (Output)		
Froth	86.6	87.6
Sludge	10.8	7.8
Sand	2.6	4.6
Oil Recovered, Wt% On Tar Sand On a Water Free Basis	9.2	11.7

(1) Calculated from slurry charge and oil and solids recovered from sample.

Table 6-5

Preliminary Study of Processability of Tar Sand from Core 22A-7

Laboratory Technique: Beaker and Spatula, Mixing for 2 Minutes at 180°F, Aeration at 0.24 SCF/HR/LB Tar Sand for 5 Minutes, 20% Water in Mixing and 50% Water in Flooding

Experiment No.	**#3**	**#4**	**#10**	**#11(1)**	**#12**
Core Depth Feet	15-23	23-32	32-42	42-47	47-52
Material Recovery, Wt % (Water Free Basis)	96.1	99.0	99.0	103	98.6
Froth Composition, Wt %					
Water	45.5	27.5	26.3	34.5	31.5
Solids	22.7	15.3	7.6	15.1	15.2
Oil	31.8	57.2	66.1	50.4	53.3
Yield, Wt % (Water Free Basis)					
Froth	1.7	5.7	9.9	20.0	8.2
Sludge(2)	95.8	88.1	18.0	1.5	67.7
Sand	2.5	6.2	72.1	78.5	24.1
Oil Recovery, Wt % (Input)					
Froth	21.8	69.1	83.5	96.8	53.2
Sludge	77.5	27.6	7.5	0.9	40.6
Sand	0.7	3.3	9.0	2.3	6.2
Oil in Tar Sand Feed, Wt %	4.1	6.1	10.1	12.8	11.3

(1) Assumed error in wet froth weight and prorated accordingly

(2) Dilution prior to decanting was not used in any of these tests

Table 6-6

Comparision of Laboratory Dense Phase Extractions of Spot Samples Taken from Area "D" in the Area of Auger Hole No. 9

Experiment - D 31	1	2	3	4	5	6	7	8
Area of Sampling	"B"	"D"						
	Cut From Large Lump	9 x 2 Auger Hole,5-10' 14' North-East	10' East	Hand Dug	10' East	9 x 1 Auger Hole,5-10' Hand Dug Sample	Area D Sample Rec'd Sarnia	9 x 2 Auger Hole,5-10' 5' East
Tar Sand History	Blasted	Undisturbed				Disturbed	-	Undisturbed
Tar Sand Composition, Wt %								
Water	1.6	1.8	2.4	6.8	6.3	6.5	6.5	1.7
Solids	87.0	83.9	83.2	86.4	90.2	84.7	83.5	84.8
Oil	11.4	14.3	14.4	6.8	3.5	8.6	10.0	13.5
Froth Composition, Wt %								
Water	32.3	38.5	34.6	45.1	48.6	52.5	39.7	49.5
Solids	16.4	14.4	5.0	17.2	10.0	15.5	10.3	7.4
Oil	51.3	47.1	60.4	37.7	41.4	32.0	50.0	43.1
Yields, Wt % (Water Free Basis)								
Froth	14.0	18.8	13.5	4.6	2.3	3.6	4.9	15.0
Sludge	6.4	1.1	5.7	9.6	3.2	13.0	10.8	1.4
Sand	79.6	80.1(1)	80.8	85.8	94.5	83.4	84.3	83.6
Oil Recovery in Froth Wt % (Input)	95.6	99.0	84.7	42.7	50.9	26.0	38.5	92.9

(1) All sand passed a 40 mesh U.S. Sieve.

In general, the agreement in the results indicates that auguring does not affect processability significantly, at least with tar sands of the type tested. The agreement is quite remarkable when considering that the augured samples were tested at Mildred Lake using an improvised heating system, and the hand dug samples at Sarnia after transportation in sealed cans. The indication is that tar sand samples are fairly stable over short periods of time, and the processability of tar sands is not affected significantly if samples are sealed to minimize air in storage at about 40°F.

6-5 Behaviour of Blends

Two similar series of exploratory experiments were carried out in which the amount of a poor quality Area "D" tar sand was varied in a blend with an Area "B" tar sand.

(a) Separation Series I

In the first series a sample of poor quality tar sand from Area "D", general location of Auger Hole 9, was blended with a better quality tar sand from Area "B". The results are summarized in Table 6-8 and are plotted in Figure 6-3. It will be noted that the Area "B" tar sand gave poorer results (83% oil recovery) than usually obtained with Area "B" tar sand, i.e. 96%. The oil loss is not to sludge, but is associated with the sand. This could result from either not enough mixing, or more likely from dried out surface tar sands taken with the sample from the formation. The latter explanation is probably more correct as this observation has been made many times before on oil-sand mixtures that require a great deal of energy to separate.

In general, a linear relationship is indicated for froth compositions, yields and oil recoveries with blend composition, Figure 6-3. However, a small synergistic effect on oil recoveries might be indicated at the higher concentrations of Area "D"-1 tar sand in the blend. Tar sand compositions calculated from material balances show good agreement with analyses.

(b) Separation Series II

In the second series, a sample of poor quality tar sand from Area "D" was blended with a sample of good quality tar sand from Area "B". The latter sample had been in storage for 10 months and had probably "aged". This is substantiated to some extent by the larger oil loss to sludge. The data is summarized in Table 6-9. Again, a linear relationship with blend composition is indicated for froth composition, yields and oil recoveries, Figure 6-4. Further, good agreement between calculated tar sand compositions and analyses was also found.

Although there is some deviation in the data, in general there appears to be linear relationships between processability and blend composition. Thus, *each type of composition (i.e. tar sand) in a blend appears to behave independently.* These preliminary results are very important as they indicate that processability studies on a large representative homogenized amount of tar sands would give an overall definition of the area. Further, small scale processability tests of homogenized core sections might be integrated to define the processability of an immediate location, which in turn could be integrated to give an overall estimate of processability for an area or section. This definition of processability would also be achieved at only a fraction of the cost required to carry out a similar evaluation on a pilot plant scale.

6-6 Effect of Freezing

In this example, four separations were carried out before and after three consecutive freezings and thawing of a sample of tar sand. The sample of tar sand was taken immediately on arrival from a large shipment received at Sarnia early in January 1962. Its' history was unknown. It was not frozen at the time of sampling.

In these separations the froth from flotation was collected separately from that collected after aeration.

The air addition in these separations was about 3.5 SCF/hr/lb of tar sand, but rate control was only approximate. Mixing, stirring and aeration were carried out in the same time sequence in each experiment.

The results of these preliminary experiments are summarized in Table 6-10. Comparison of the total froth compositions indicates that the water content decreases with consecutive freezings. However, the solids content decreases after the first freezing, and increases with consecutive freezings. The yields of froth from flotation appear to decrease and those from aeration ap-

Figure 6-2

Oil Recovery Is General Function of Tar Sand Grade

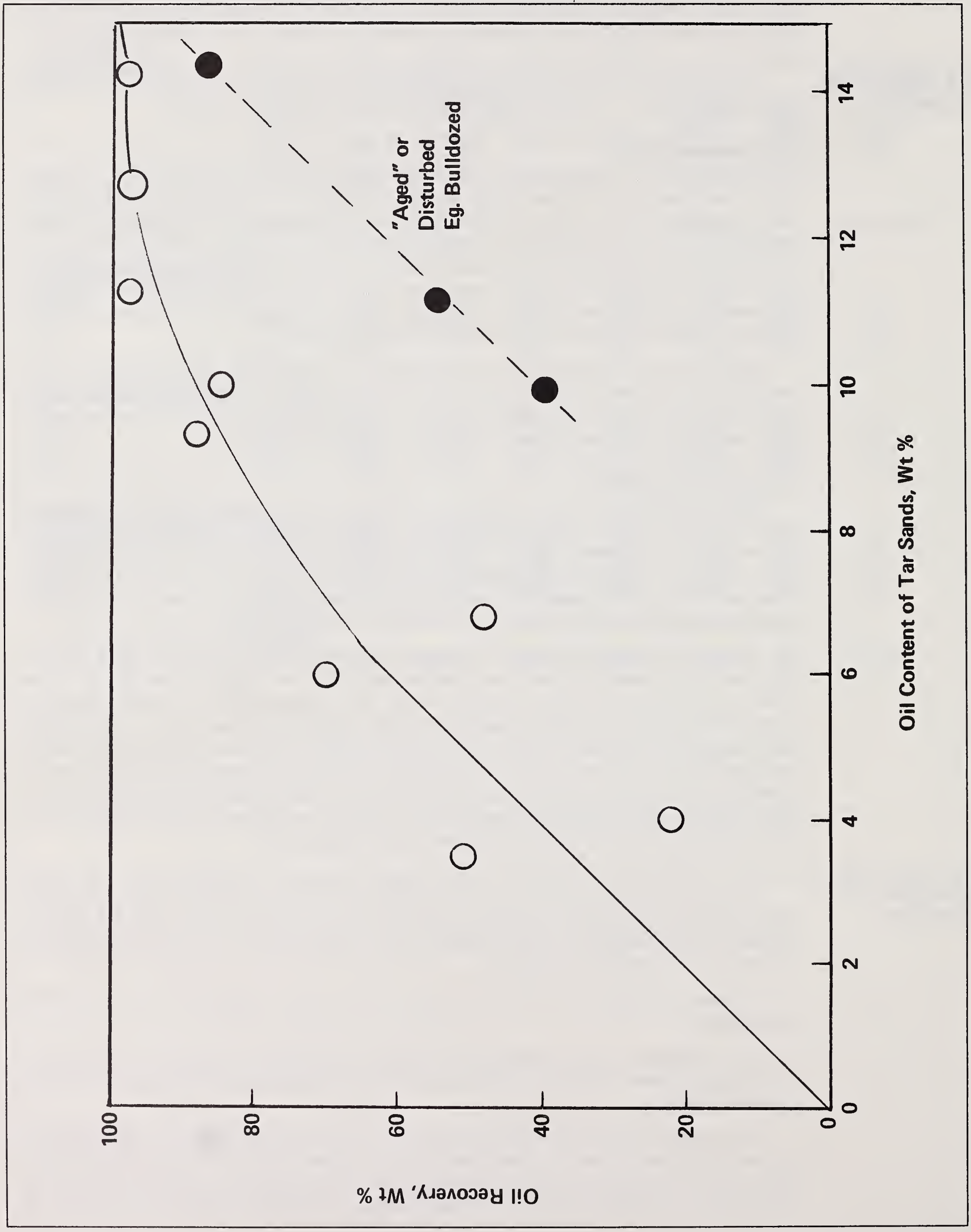


Table 6-7

Laboratory Extraction Comparision of Augered and Hand Dug Samples of Tar Sands from the Sample Location

Experiment	#15(1)	#37	#16(1)	#38
Carried Out at	Mildred Lake	Sarnia	Mildred Lake	Sarnia
Date - 1962	Apr. 17	May 10	Apr. 17	May 10
Sample Designation	Augered	Hand Dug	Augered	Hand Dug
	9 x 1 Hole, 5-10'		9 x 2 Hole, 5-10'	
Tar Sand History	Disturbed 1-1/2 years ago		Undisturbed	
Froth Composition, Wt %				
Water	54.3	52.5	47.7	45.1
Solids	13.6	15.5	11.9	17.2
Oil	32.1	32.0	40.4	37.7
Yields, Wt % (water free basis)				
Froth	3.9	3.6	5.0	4.6
Sludge	29.9(2)	13.0	34.4(2)	9.6
Sand	66.2	83.4	60.6	85.8
Oil Recovery, Wt % in (Output)				
Froth	32.5	26.6	47.0	47.0
Sludge	61.8(2)	60.4	51.1(2)	29.4
Sand	5.7	13.0	1.9	23.6

(1) Spot sample taken from homogenized large batch.
(2) Dilution prior to decanting was not used in these tests.

pear to increase. The solids content of the latter also increases with consecutive freezings. It is interesting that the sand becomes cleaner, i.e. contains less oil, with consecutive freezings of the tar sand feed. Perhaps this is a result of the expansion of the water films around the sand particles on freezing, enhancing this aspect of separation.

In general, these preliminary results tentatively suggest that a single freezing of a sample of tar sand similar to that used in this study will give approximately similar process results to those obtained before freezing. Further freezings and thawing of tar sand, however, appear to cause gradual deterioration of the ability of the oil to float. Perhaps the clay in the water films is coming out of suspension and attaching to the surface of the oil particles. This indicates that the processability of tar sands that undergo successive freezings and thawing, that is above the frost line or after mining, will deteriorate over the years, although clean sand will separate in a hot water flotation process, oil recoveries will be low.

6-7 Fines-Mixing Intensity

The combined effects of fines in separation with different intensities of mixing was studied using a modified beaker technique that substituted a mortar and pestle for the beaker and spatula to change the mixing intensity. The results are summarized in Tables 6-11 and 6-12.

The oil recoveries in the froth for the two different mixing intensities are plotted in Figure 6-5 against the amount of fines in the system. Mild mixing with aeration in separation gave good oil recoveries, that appeared to increase slightly with increasing fines in the system, Figure 6-5. More severe mixing, however, showed the same effect, that is up to 25 wt% of total mineral matter. At higher fines contents in the system, poorer oil recoveries in the froth were obtained with oil loss to the sludge. The reason for this result is not obvious; perhaps mechanical flocculation of clay occurred occluding oil, which now sank as sludge, or a water wet clay film was mechanically formed around some oil particles, which now prevented the attachment to air bubbles introduced in the separation. However, the performance under low shear-high clay conditions support the need for low optimum energy input.

The composition of the froths for the different mixing intensities are plotted against the amount of fines in the system in Figure 6-6. In general, both the solids and water content appear to be independent of the amount of fines in mixing. Severe mixing, however, results in a significantly higher water content. This suggests that emulsification of oil and water occurred in severe mixing. Thus, the amount of mechanical energy input into the process can be critical at some point.

(a) Mixing Intensity

A plot of the weight ratios of solids to oil and water to oil in froth shows more clearly the effect just discussed, Figure 6-7. The apparent horizontal locus of the data indicates that the solids in the froth is a function of the tar sands quality; presumably it is oil-wet clay and/or partially oil-wet clay content. Further, it might be postulated that this same clay is responsible to some extent for sludge formation in solvent dilution and separation. The vertical division of the two sets of data show that more severe mixing results in emulsification of additional water with oil. The results plotted in Figure 6-7 are also compared with those obtained by Clark. It will be noted that there is both a significant difference in solid content of the froths and oil recovery between the two sets of data with and without aeration.

These observations lead to a better understanding of the process. By comparing these data it can be seen that no aeration in separation gives lower oil recovery in oil in the froth, that has lower solids concentrations, than operations with aeration, Table 6-13. It appears that aeration facilitates the flotation of incremental froth with high solids concentrations.

There are some discrepancies in the water content of the froth: the water content of a froth from hot water separation which is normally about 37 wt% can be reduced to about 25 wt% or less by cooling and draining the water containing some solids; particularly if it is mixed at the same time as draining. The low values of water content that have been found in some operations may either result from this source of error or be associated with milder mixing operations as discussed above. The apparent minimum water content of about 25 wt% may however be difficult

Table 6-8

Summary of Laboratory Dense Phase Separation Results (Series I) with Blends of Tar Sands from Area "B" and "D"

Experiment No. 10	(i)	(ii)	(iii)	(iv)	(v)
Tar Sand Blend, Wt %					
Area "B"-1	100	75	50	25	0
Area "D"-1	0	25	50	75	100
Tar Sand Composition, Wt %					
Water	4.2	5.3	7.9	10.1	12.5
Solids	84.0	82.7	81.1	80.2	78.1
Oil	11.8	12.0	11.0	9.7	9.4
Froth Composition, Wt %					
Water	22.2	22.6	29.3	34.4	32.4
Solids	15.9	16.7	11.6	10.7	10.8
Oil	61.9	60.7	59.1	54.9	56.8
Yields, Wt % (Water free basis)					
Froth	13.9	11.2	7.4	5.5	5.6
Sludge	5.7	5.6	13.0	12.7	14.4
Sand	80.4	83.2	79.6	81.8	80.0
Oil Recoveries, Wt % in (Output)					
Froth	82.6	70.7	51.1	41.1	43.7
Sludge	3.6	6.9	38.4	46.0	47.5
Sand	13.8	22.4	10.5	12.9	8.8
Tar Sand Composition, Wt % (Based on Material Balance)					
Water(1)	3.5	5.5	8.2	9.7	11.4
Solids	83.6	82.7	80.7	80.1	79.0
Oil	12.9	11.8	11.1	10.2	9.6

(1) 100 - Wt % oil and solids recovered ≅ water content.

Figure 6-3

Laboratory Dense Phase Separations (Series I) of Blends of Poor Quality Area "D" and an Area "B" Tar Sands

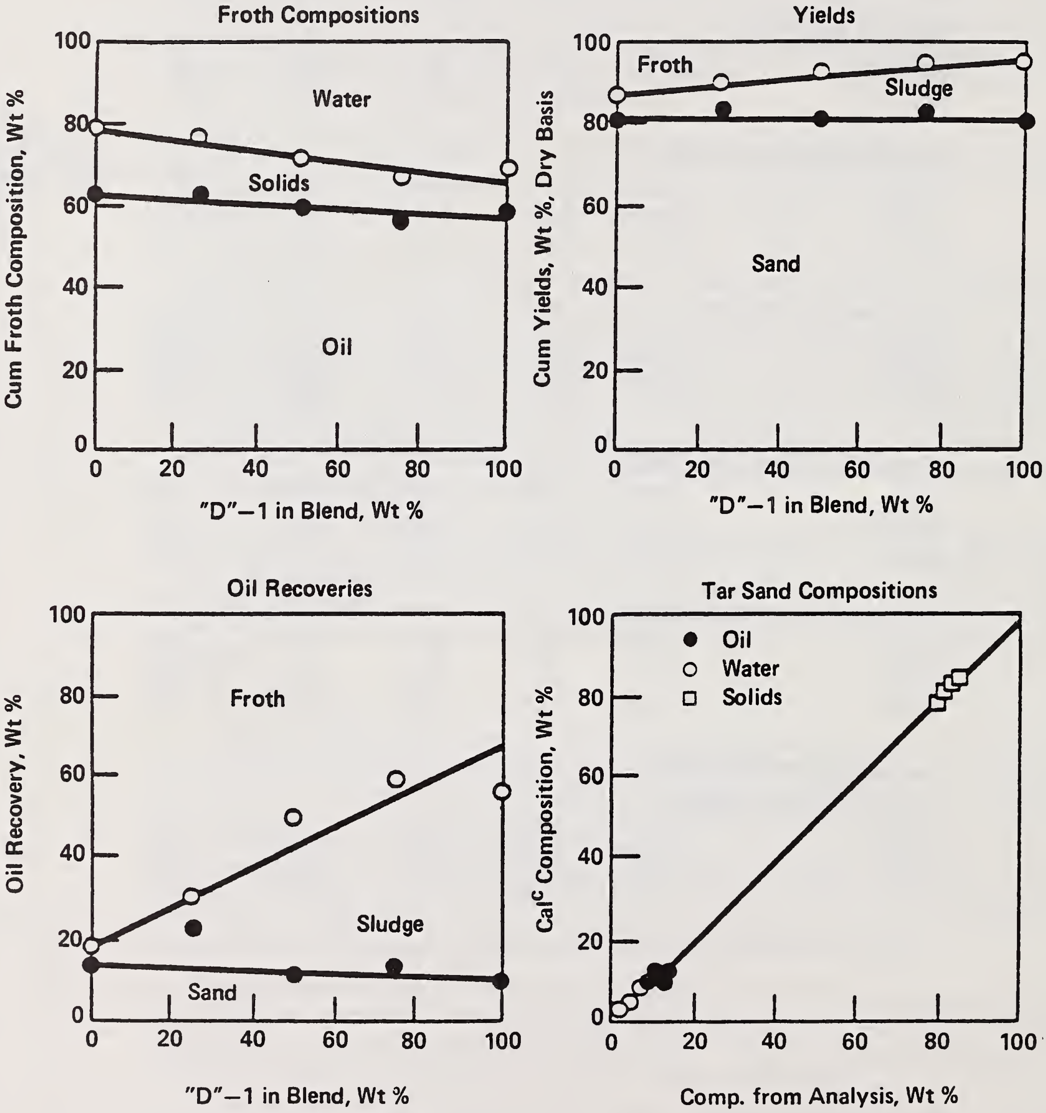


Table 6-9

Summary of Laboratory Dense Phase Separation Results (Series I)I with Blends of Tar Sands from Area "B" and "D"

(Area "B" Tar Sand had been in storage for 10 months - aged)

Experiment No. 12	**(i)**	**(ii)**	**(iii)**	**(iv)**	**(v)**
Tar Sand Blend, Wt %					
Area "B"-2	100	75	50	25	0
Area "D"-2	0	25	50	75	100
Tar Sand Composition, Wt %					
Water	4.9	7.7	9.1	11.5	12.9
Solids	78.9	79.3	78.5	79.0	78.5
Oil	16.2	13.0	12.4	9.5	8.6
Froth Composition, Wt %					
Water	25.4	29.1	26.3	31.7	36.7
Solids	7.6	9.5	9.6	13.5	14.3
Oil	67.0	61.4	64.1	54.8	49.0
Yields, Wt % (water free basis)					
Froth	14.2	8.0	7.7	5.7	2.8
Sludge	6.6	13.6	15.3	16.0	22.0
Sand	79.2	78.4	77.0	78.3	75.2
Oil Recoveries, Wt % in (Output)					
Froth	73.8	44.5	55.4	38.8	27.2
Sludge	18.8	47.5	34.3	50.4	58.4
Sand	7.4	8.0	10.3	10.8	14.4
Tar Sand Composition, Wt % (Based on Material Balance)					
Water	5.2	6.7	9.9	10.8	14.4
Solids	78.4	78.8	79.2	78.6	78.7
Oil	16.4	14.5	10.9	10.6	6.9

(1) 100 - Wt % oil and solids recovered ≅ water content.

Figure 6-4

Laboratory Dense Phase Separations (Series II) of Blends of Poor Quality Area "D" and an Area "B" Tar Sands

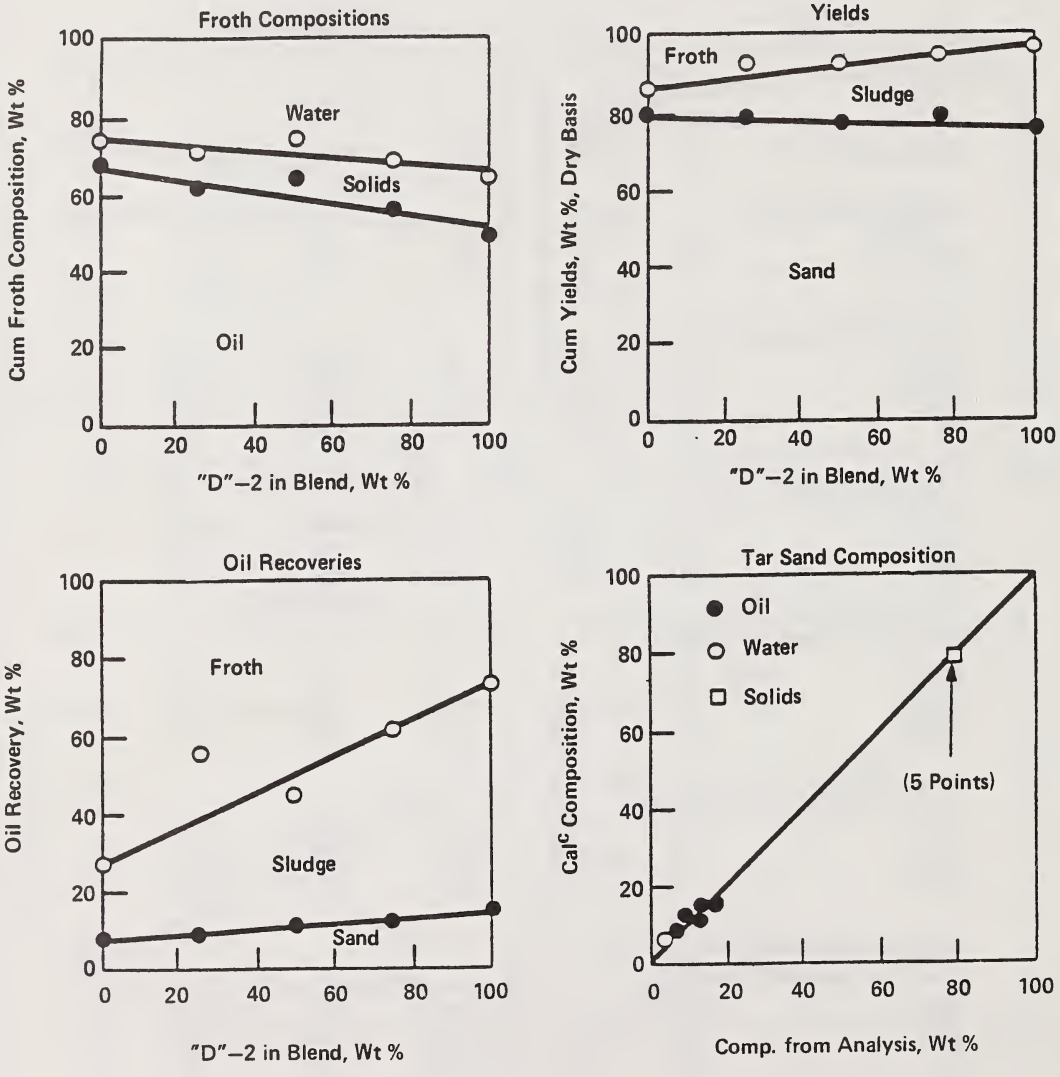


Table 6-10

Preliminary Results on Effect of Freezing Tar Sand Feed prior to Separation in a Dense Phase Operation

Conditions: Tar Sand contained 2.2% Water, 11.7% Oil, 86.1% Sand, 180°F, 20 Wt % Water in Mixing, 2 minutes Mixing in a Beaker with a Spatula, 80 Wt % Water in Separation, 3 consecutive Oil Skimmings followed by 3 Consecutive Skimmings after Aeration.

Experiment No.	**2102**	**2103**	**2106**	**2107**
Tar Sand Treatment	**As received at Sarnia, Unknown History**			
1st Freezing(1), hr	-	91	91	91
2nd Freezing(1), hr	-	-	40	40
3rd Freezing(1), hr	-	-	-	41
Material Balance(2) Wt %	98.3	97.8	99.0	99.9
Froth Composition, Wt % (From Skimming)				
Water	41.2	40.2	32.9	27.8
Solids	11.6	6.7	8.9	10.5
Oil	47.2	53.1	58.2	61.7
Froth Composition, Wt % (From Aeration)				
Water	50.0	42.9	37.0	33.9
Solids	12.5	14.3	13.0	19.4
Oil	37.5	42.9	50.0	46.8
Total Froth Composition, Wt %				
Water	42.4	40.7	33.9	29.5
Solids	11.6	7.9	9.9	12.9
Oil	46.0	51.4	56.3	57.6
Yields(2) Wt % in				
Froth (Skimmings)	12.2	11.2	10.1	12.0
Froth (Aeration)	1.2	2.1	3.0	4.2
Sludge	6.8	6.1	7.3	3.4
Sand	79.8	80.7	79.5	80.4
Oil Recoveries, Wt % in				
Froth (Skimmings)	83.2	82.3	73.0	75.2
Froth (Aeration)	7.9	13.0	19.7	21.8
Sludge	4.9	2.9	5.5	1.8
Sand	4.0	1.8	1.8	1.1
Oil Balance, Wt %	96.5	98.6	99.6	113.6(3)
Solids Balance, Wt %	98.5	97.7	98.9	98.0

(1) Temperature of Freezer was -4°F.

(2) Water free basis.

(3) High - probably because of not enough oven drying of froth for water content before ashing. Soxhlet extraction of froth is now used to avoid this type of error experienced in the past.

Table 6-11

Effect of Clay and Mixing in Hot Water Separation with Aeration (Tar Sand contained 1.7 Wt % Oil, 2.2 Wt % Water, 80.4 Wt % Sand, 5.7 Wt % Clay)

Experiment No.	21S2	21S2a	21S2b	21S2c	21S2d	21S2e
Conditions						
Additions in Mixing, Wt %(1)						
Clay(1)	0	9	18	27	36	45
Water	15					
Temperature, °F	180					
Type of Mixing	Mild (Beaker and Spatula)					
Premixing Time, min.	2					
Flooding Water, Wt %	85					
Number of Aerations	3					
Duration of Aeration, min.	1					
Air Rate, SCF/hr/lb Tar Sand	0.5					
Sand Washing	No	Yes	Yes	Yes	Yes	Yes
Results, Wt %						
Material Recovery	97.6	99.8	99.7	98.7	99.1	100.7
Yield of Oil Froth	16.3	18.3	19.0	20.1	19.2	23.6
Sludge	4.7	5.4	11.3	18.4	15.1	18.4
Sand	79.0	85.3	87.7	88.5	101.8	103.0
Composition of Oil Froth						
Water	29.6	25.2	27.5	25.0	29.1	20.5
Solids	14.5	18.1	15.1	18.9	14.3	17.4
Oil	55.9	56.7	57.4	56.1	56.6	62.1
Oil Content of						
Sludge(2)	1.32	3.07	2.33	0.94	0.34	0.56
Sand(3)	0.73	0.60	0.36	0.40	0.16	0.28
Sand(4)	0.68	0.55	0.32	0.42	0.26	0.30
Oil Recovery in						
Froth	93.8	94.2	95.3	95.4	97.2	97.3
Sludge	0.7	1.5	2.3	1.5	0.5	0.7
Sand	5.5	4.3	2.4	3.1	2.3	2.0

(1) Wt % on Tar Sand.
(2) Based on Ash Determinations.
(3) Based on Soxhlet Extractions.
(4) Oven dried basis.

Table 6-12

Effect of Clay and Mixing in Hot Water Separation with Aeration (Tar Sand contained 11.7 Wt % Oil, 2.2 Wt % Water, 80.4 Wt % Sand, 5.7 Wt % Clay)

Experiment No.	**21S3**	**21S3a**	**21S3b**	**21S3c**	**21S3d**	**21S3e**
Conditions						
Additions in Mixing, Wt %(1)						
Clay(2)	0	9	18	27	36	45
Water	15					
Temperature, °F	180					
Type of Mixing	More Severe (Mortar and Pestle)					
Premixing Time, min.	5					
Flooding Water, Wt %(1)	85					
Number of Aerations	3					
Duration of Aeration, min.	1					
Air Rate, SCF/hr/lb Tar Sand	0.5					
Sand Washing	No	Yes	Yes	Yes	Yes	Yes
Results, Wt %						
Material Recovery	97.0	97.6	98.5	98.8	98.6	10???
Yield of Oil Froth	16.7	16.8	19.6	17.5	16.7	2???
Sludge	2.4	6.4	5.7	12.5	16.7	13.3
Sand	80.9	85.8	92.7	97.0	102.6	111.8
Composition of Oil Froth						
Water	33.9	32.7	33.0	32.5	40.4	33.7
Solids	16.1	14.9	14.9	14.3	13.3	14.1
Oil	50.0	52.4	52.0	53.2	46.3	52.2
Oil Content of						
Sludge(3)	0.7	0.0	0.0	5.9	7.4	9.6
Sand(4)	0.53	0.36	0.38	0.29	0.89	0.34
Sand(3)	0.40	0.38	0.26	0.26	0.68	0.34
Oil Recovery in						
Froth	95.4	96.5	97.1	90.3	79.1	86.2
Sludge	0.3	0	0	7.1	12.6	10.6
Sand	4.3	3.5	2.9	2.6	8.3	3.2

(1) Wt % on Tar Sand.
(2) Oven dried basis.
(3) Based on ash determinations.
(4) Based on Soxhlet extractions.

to obtain in a hot water commercial separation using aeration unless special mechanical separation equipment is used.

Alternatively, omitting aeration from the separator, but using this technique in a separate treatment of the water stream would presumably accomplish the same overall froth quality and oil recovery.

(b) Comparison of Results

There is an inconsistency between the two sets of results on the effect of clay. In the first set of experiments, without aeration, the effect of clay was to increase the amount of sludge, presumably by increasing the clay content of some oil which now sinks, Figure 6-1. This indicates that if aeration had been used, the solids content of the froth would increase with clay content. The clay used in these experiments was part of a large separate lens or pocket taken from the formation. In the second set of experiments essentially no effect of clay on froth composition was found. The clay used here was an homogenized mass of small, water-wet clay pockets hand picked from a sample of tar sands. *It appears that the "state" of the clay can have a substantial effect on its behaviour.*

It is not likely that the difference between these two sets of data can be explained in terms of aeration. Rather the data indicates that there are other effects for investigation, such as types or surface state of clay from adsorbed polyvalent ions, or the effect of mixing with steam. The consistency within the set of data using this modified experimental method, however, shows the power of this experimental technique to investigate the effect of variables.

The main conclusion of these preliminary studies is that premixing can cause emulsification of water in the oil froth. The water content of the froth can hence be reduced by milder mixing with water addition to aid coalescence prior to water separation.

Table 6-13

Froth Quality from Hot Water Separations with Good Quality Tar Sands

Aeration(1)	No				Yes			
Data Source	Clark	C.S.A.		Imperial	C.S.A.			Imperial
	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(4) (10)
No. of Points Averaged	7	34	26	2	50	20	8	2
Froth Composition								
Water, Wt %	35	23	36	37	37	34	27	38
Solids, Wt %	4	6	6	4	11	14	10	10
Oil, Wt %	61	71	58	59	52	52	63	52
Oil Recovery, Wt %	77	75	88	80	97	93	90(9)	98

(1) In Wash Tank or Stripper-Separator.
(2) Canadian Oil and Gas Industries, Sept. 1950.
(3) Pilot Plant Run 10, C.S.A. Status Summary Report - Feb. 1961.
(4) Bench Unit, C.S.A. Status Summary Report - Jan. 1961.
(5) Results of Beaker Experiments.
(6) "Modified Dense Phase" - Pilot Plant Run 11. C.S.A. Status Summary Report - July 1961.
(7) Core Samples - Bench Unit Series 1005. C.S.A. Status Summary Reports - Sept. 1961 and Jan. 1962.
(8) Core Samples - Bench Unit Series 1008 - Process Meeting - Jan. 1962.
(9) Average of Two Points.
(10) Feed - sample of that used in Pilot Plant Run 11. See note (6).

Figure 6-5

High Clay and Severe Mixing with Aeration Give Poor Oil Recoveries (Tar Sand Contained 11.7 Wt % Oil, 2.2 Wt % Water, 80.4 Wt % Sand, and 5.6 Wt % Clay)

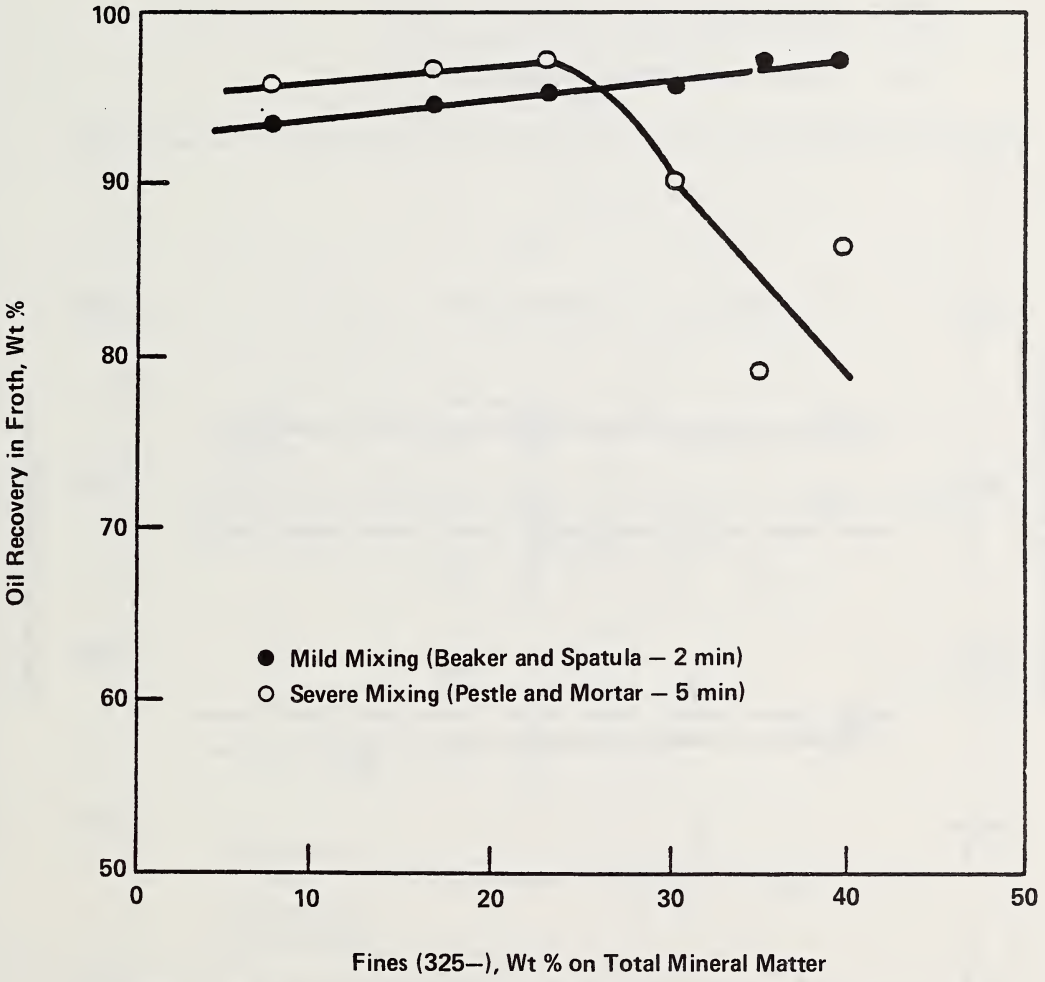


Figure 6-6

More Severe Mixing Emulsifies Water in Froth, and Froth Composition Is Independent of Added Clay (Tar Sand Contained 11.7 Wt % Oil, 2.2 Wt % Water, 80.4 Wt % Sand, and 5.7 Wt % Clay)

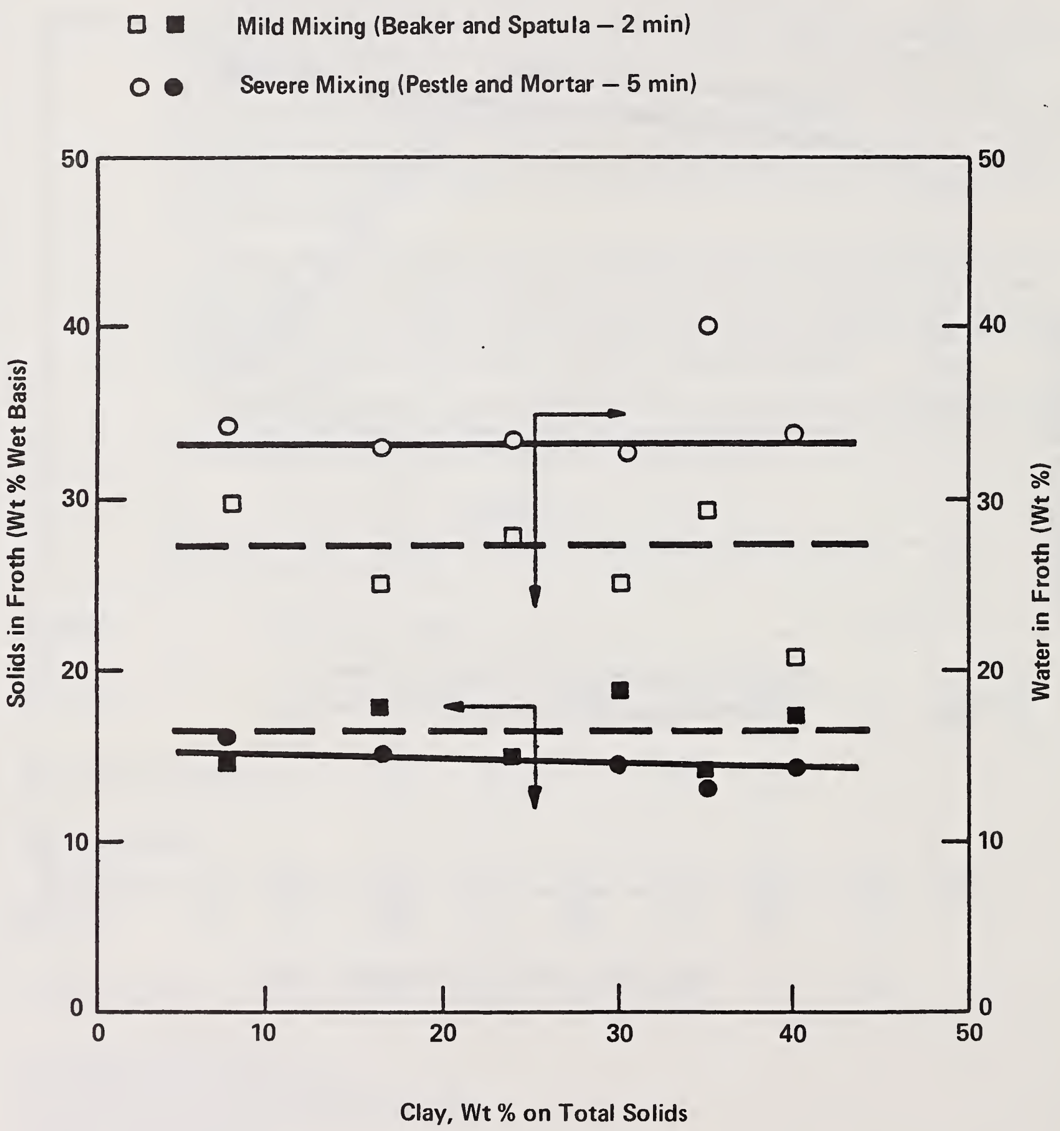
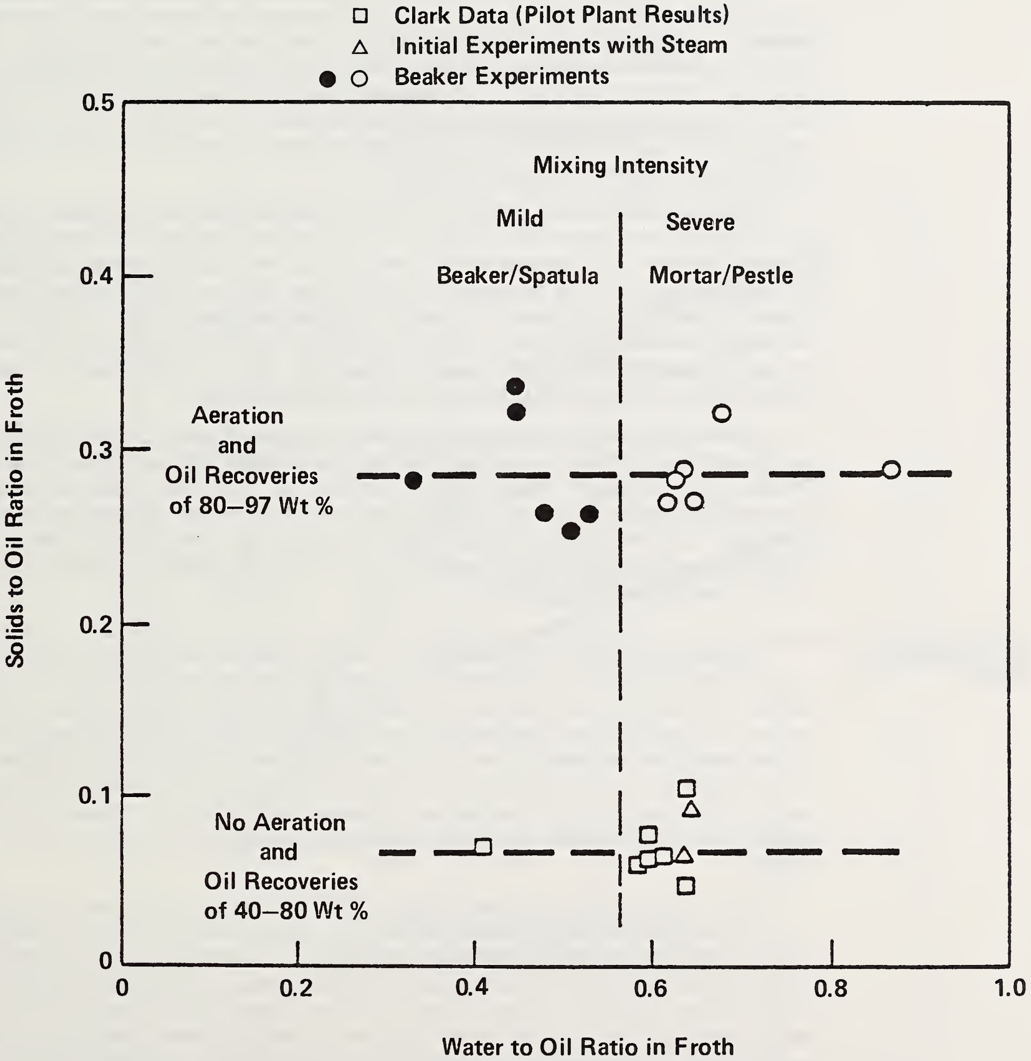


Figure 6-7

More Severe Mixing Emulsifies Water in Froth, and Solids Content Is Independent of Mixing and Aeration (Clay Addition and Aeration Experiments) (Tar Sand Contained 11.7 Wt % Oil, 2.2 Wt % Water, 80.4 Wt % Sand, and 5.7 Wt % Clay)*



*At Least 95% Passes a 325 US Mesh Sieve

6-8 Multiple Skimmings

As a survey of results showed that air addition improves oil recovery with good quality tar sands but results in higher solids in the froth, a short study was undertaken to evaluate the effects in separation of skimming, aeration time and rate. In these separations a mild and constant premixing in all operations with an Area B type tar sands was maintained. The objective was to define how air might best be used.

(a) Progressive or Staged Skimming of Froth

The plot of cumulative oil recovery in froth against separation time is shown in Figure 6-8, and the results summarized in Table 6-14. It will be noted that a maximum oil recovery obtainable by progressive or staged skimming with this Area B tar sands was just less than 90 wt%. In the experiment no further oil separation occurred when stirring up to 15 minutes. In single skimmings, oil particles surrounded by water arriving at a froth-water interface have to coalesce with the oil froth. This coalescence is slow, as indicated by the lower curve in Figure 6-8. Progressive or staged skimming of froth resulted in better oil recoveries in a given separation time than those obtained with single skimmings.

The effect of aeration rate on oil recoveries in separations is shown in Figure 6-9. Following the plot for the lower aeration solid circles, it can be seen that with half-minute skimmings up to 2 minutes, the rate of oil recovery was the same as progressive skimmings with no air, Figure 6-8. When aeration time was increased to 3 minutes, the final rate of oil recovery was lower, Figure 6-9 than that for progressive skimmings. Although the final oil recovery after 8 minutes was higher, the result at this low air rate is significantly better than that of single skimmings in the same separation time without aeration, Figure 6-8. This is an advantage for continuous operation rather than the batch technique used to evaluate this effect.

Following the plot for the higher aeration rate in Figure 6-9 shown by the closed squares, it can be seen that initially a lower oil recovery was obtained with a two minute skimming. However, with progressive aeration time of one-half, one, and three minutes the rates of oil recoveries decreased respectively, but the overall rate of oil recovery in time was significantly improved. Thus, froth recovery takes longer when lower air rates are used in separation, as would be expected. Multi stages of separation may also realize higher oil recoveries, especially in larger scale continuous operations.

6-9 Aeration Rate

The results of a series of separations in which aeration rate and duration were varied are summarized in Table 6-15. Froth compositions change with aeration time, Figure 6-10, but the amount of water in the froth appears to increase only very slightly with increasing air rate. This indicates that the agitation accompanying the aeration is the prime cause of the increase of water content in the froth with aeration time. The higher solids content of the froth at the higher air rate of 3.0 SCF/hr/lb tar sand may be due to the higher air rates or to loss of water in storage of the sample. The overall yield does not appear to change with aeration time, Figure 6-11, although there is an increase in froth yield due to an increase in solids content, when the air rate was highest.

These points are also illustrated in Figure 6-12. In the upper plot, it can be seen that the water to oil ratio in the froth increases rapidly with aeration time, but only very slightly with aeration rate. The plot at the bottom of the figure shows that the sum of the oil and solids wt% recovered from the tar sand increased after 2-1/2 weeks storage in a small can at laboratory conditions. This may be due to water loss from the tar sand structure which condensed on the walls and lid of the can. The centre plot shows that there is a slight increase in solids to oil ratio with water loss from the tar sand. As ash measurements were not carried out in all experiments, only a few oil recoveries in the froth were computed. In general, they were all high and did indicate a tendency to increase with aeration time.

These preliminary studies with an Area B tar sand show that much longer times of separation with a single skimming of froth without aeration are required to effect equivalent oil recoveries obtained by (a) progressive skimming, without aeration, and (b) aeration, even at low rate 0.5 SCF/hr/lb tar sand. Final oil recovery with aeration is higher than that obtained with

Figure 6-8

Progressive Skimmings Improve Oil Recoveries in a Given Separation Time (Tar Sand Contained 11.7 Wt % Oil, 2.2 Wt % Water, 80.4 Wt % Sand, and 3.7 Wt % Clay)**

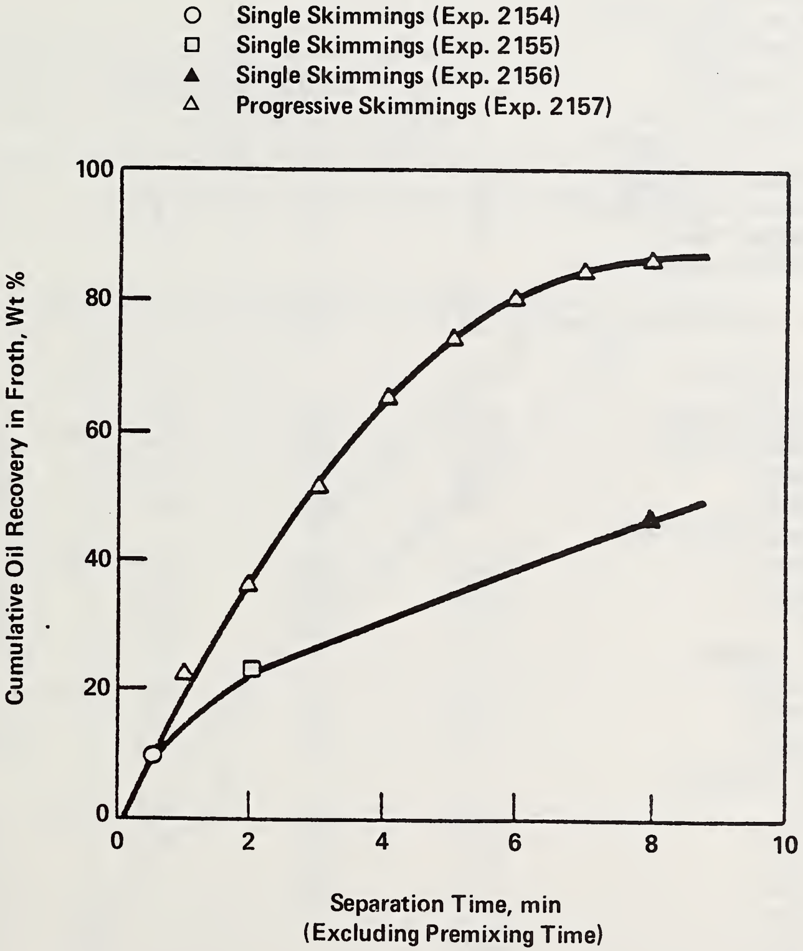


Table 6-14

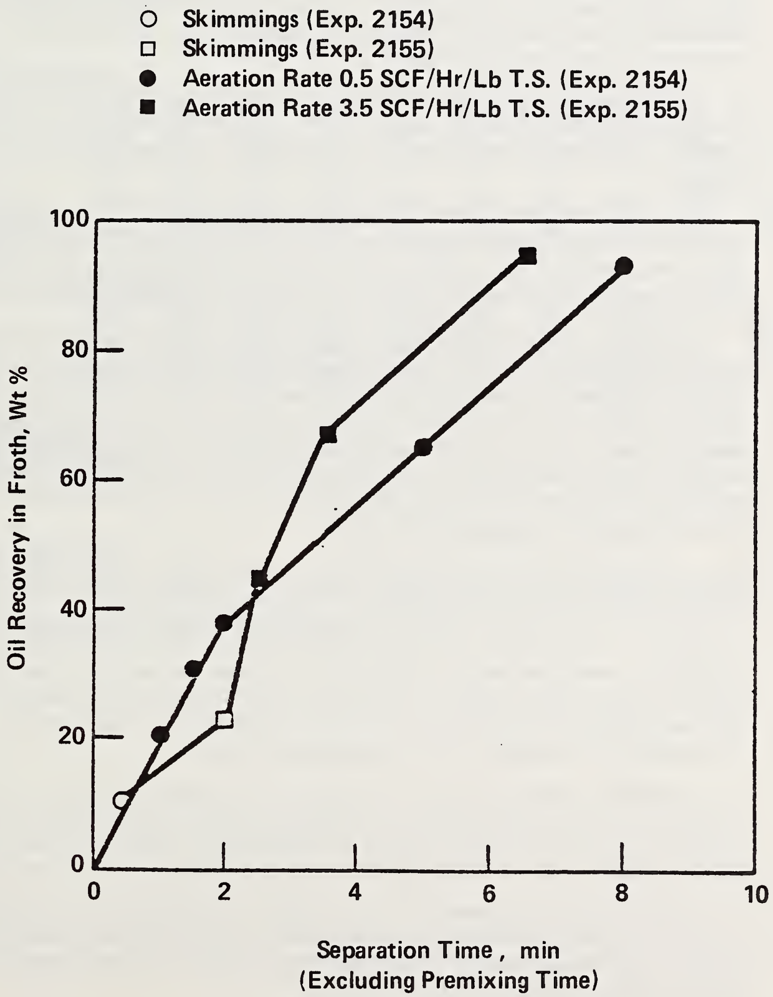
Effect of Skimming and Aeration in Hot Water Separations (An Area B Tar Sand containing 11.7 Wt % Oil, 2.2 Wt %Water, 80.4 Wt % Sand and 5.7 Wt % Clay)

Experiment No.	**2154**	**2155**	**2156**	**2157**
Symbols[(1)] in Figures 8 and 9	● ○	□ ■	◊	Δ
Conditions				
Water in Mixing, Wt %$^{(2)}$	15			
Temperature, °F	180			
Type of Mixing	Mild (Mortar and Spatula)			
Premixing Time, min.	2			
Flooding Water, Wt %$^{(2)}$	85			
Number of Skimmings	1	1	1	8
Duration of Skimmings, min.	1/2	2	8	1
Number of Aerations	5	3	-	-
Duration of Aerations, min.	1/2,1/2,1/2,3,3	1/2,1,3	-	-
Air Rate, SCF/hr/lb Tar Sand	0.5	3.6	-	-
Results, Wt %				
Material Recovery	99.1	100.7	95.8	97.8
Yields of Oil Froth	15.9	17.9	7.9	17.0
Sludge	4.5	2.3	5.4	2.6
Sand	79.6	79.8	86.7	80.4
Composition of Froth				
Water	36.5	28.2	22.6	25.9
Solids	16.5	15.5	14.9	20.5
Oil	47.0	56.3	62.5	53.6
Oil Content of				
Sludge$^{(3)}$	27.7	13.6	32.9	7.1
Sand$^{(4)}$	0.9	0.4	4.3	1.7
Sand$^{(3)}$	1.0	0.7	4.3	1.2
Oil Recovery in				
Oil #1	9.3	24.1	47.2	24.2
Oil #2	10.5	21.2	-	11.7
Oil #3	10.0	21.7	-	15.8
Oil #4	8.7	27.9	-	13.3
Oil #5	27.2	-	-	9.8
Oil #6	27.3	-	-	6.0
Oil #7	-	-	-	3.9
Oil #8	-	-	-	2.7
Total Froth	**93.0**	**94.9**	**47.2**	**87.4**
Sludge	1.0	2.1	17.1	1.8
Sand	6.0	3.0	35.7	10.8

(1) Closed points indicate aeration was used in separation.
(2) Wt % on tar sands.
(3) From ash analyses.
(4) From Soxhlet analyses.

Figure 6-9

Higher Aeration Rates and Frequent Skimmings Improve Oil Recoveries in a Given Separation Time (Tar Sand Contained 11.7 Wt % Oil, 2.2 Wt % Water, 80.4 Wt % Sand, and 5.7 Wt % Clay)



even the best skimming technique, i.e. progressive or staged, and no aeration. Higher air rates give more rapid separation.

It is thought that improved oil recoveries with higher rates of aeration in separation result from (a) a larger internal air-water interface at which spreading of oil can occur below the water-froth interface, (b) coalescence of the oil particle by virtue of the oil-filming effect, and (c) either by occlusion or adherence of oil particles in the aqueous phase which are brought in contact with the water-air-froth interface. This theory indicates that air not only achieves flotation, but acts as a bridging agent to effect the coalescence of oil particles with bulk froth. The higher rate of coalescence with high air rates is consistent with this theory. Although froth is metastable, though it can be dispersed by mixing and will reform.

It is also indicated that separator design might be improved by a series of progressive skimming-aeration systems. Such a design should significantly increase throughput rates for effective froth removal and good oil recoveries. Adoption of this technique in 1962, by Cities Service Athabasca in the Bench Unit modification, based on this work, resulted in very high oil recoveries with most types of tar sands.

Increasing aeration rate only increases the water content of the froth very slightly, if at all. Increasing agitation significantly raises the water content of the froth, which is closer to the ideal condition for emulsification of water in the oil phase, i.e. low interfacial tension and high mixing intensity.

Water lost from the tar sand structure on storage cause oil-solid "wetting", which would be reflected in a higher solids content of the froth. The extreme of this case is dried tar sands that will not separate using the conventional procedure of hot water flotation with chemical addition. Hence oil sample aging is always a factor in these and any separation data.

(a) Flotation Gas

If the gas content of the oil in the tar sand could be increased, separation by flotation would be greatly facilitated. This approach to separation is particularly important for poor quality tar sands. Preliminary experiments have been carried out in which finely divided, homogenized tar sands were allowed to stand at room temperature under a pressure of ethane and also CO_2 for extended periods of days. It was postulated that solubility of gas in oil would increase processability. However, measurement of the processability of the tar sand showed little or no change, see example in Table 6-16. Oil recoveries are low even for this type of tar sands, that presumably reflects the effects of aging and/or disturbance.

A similar result was obtained in which CO_2 was substituted for air in the separation stage. Perhaps a slightly poorer result might be indicated by the experiment with CO_2, due to its' very weak acid nature in water, although CO_2 solubility in water decreases rapidly with increasing temperature. The solubility of CO_2 at 180°F is 0.016 g/100 ml of water, which is <1/50 of the solubility at room temperature (70°F). Higher pressures are needed to dissolve the CO_2 into process water to both counteract this effect and to aid flotations as the smaller the gas bubbles, then theoretically the more effective the flotation. However, the effect of dissolved or more finely divided gas in separation will also increase solids flotation.

Exploratory experiments were also carried out at atmospheric pressure to investigate any difference between air and methane as flotation gases with a Beaver Creek tar sand that does not separate well. In one comparison, the gas was introduced in mixing with water for 3 1/2 hours at 180°F to effect oxidation and saturation of the system. The results are summarized in Table 6-17.

Poorer results were obtained in the experiment with methane. It is interesting that such low oil recoveries were obtained under mildly alkaline conditions. Clearly, further studies are indicated to establish the reasons for some poor processability with some Beaver Creek Tar Sands and how high oil recoveries might be achieved.

6-10 Separation pH

The processabilities of three tar sands from Area B, and Area D, Holes 9 and 10, are shown in Table 6-18. It will be noted that excellent oil recoveries were obtained with tar sands from Area B taken from the bottom of the formation. The separations with Hole 9 and Hole 10 tar sands from Area D were not as good. Both these samples taken from near the top of the forma-

Table 6-15

Summary of "Quicky" Experiments to Show the Affect of Aeration (with mixing) Time and Air Rate in Hot Water Separation of Area B Tar Sand

Experiment No. 8	**a**	**b**	**c**	**d**	**e**	**f**	**h**	**i**	**j**	**k**	**l**	**m**
Date Carried Out	**March 13-14th**							**April 3rd**				
Conditions												
Aeration Time, min	2	4	6	8	2	4	8	2	4	6	8	2
Air Rate, SCF/HR/lb Tar Sand	0				0.5			3.0				6.0
Froth Composition, Wt %												
Water	23.4	30.3	35.4	37.6	27.1	28.4	34.8	28.6	25.6	37.0	39.4	28.6
Solids	8.8	10.4	9.9	10.3	6.9	10.4	11.5	13.2	16.2	16.0	9.2	9.6
Oil	67.8	59.3	54.7	52.1	66.0	61.2	53.6	58.2	58.2	47.0	51.4	61.8
Solids to Oil Ratio	0.13	0.18	0.18	0.20	0.11	0.17	0.22	0.23	0.28	0.34	0.18	0.16
Water to Oil Ratio	0.34	0.51	0.65	0.72	0.41	0.47	0.65	0.49	0.44	0.79	0.77	0.46
Yields, Wt % (Water Free Basis)												
Froth	15.0	15.0	14.4	15.2	13.8	14.3	14.7	16.3	16.0	15.8	17.3	13.2
Sludge	6.2	5.0	6.5	4.8	3.8	4.1	5.3	5.2	4.1	4.3	4.1	4.3
Sand	77.6	77.6	76.1	76.9	80.2	78.7	77.1	77.3	78.0	78.4	77.8	80.2
Oil Recovered in Sludge And Sand, Wt % on Total Oil	-	-	-	-	-	-	-	3.7	5.9	2.0	3.1	7.2
Oil and Solids Recovered Wt % on Tar Sand(1)	98.8	97.6	97.0	96.9	97.8	97.1	97.1	98.6	98.1	98.5	99.2	97.7

(1) 100 Wt % Oil and Solids Recovered ≅ Water Content of Tar Sand.

Figure 6-10

Froth composition

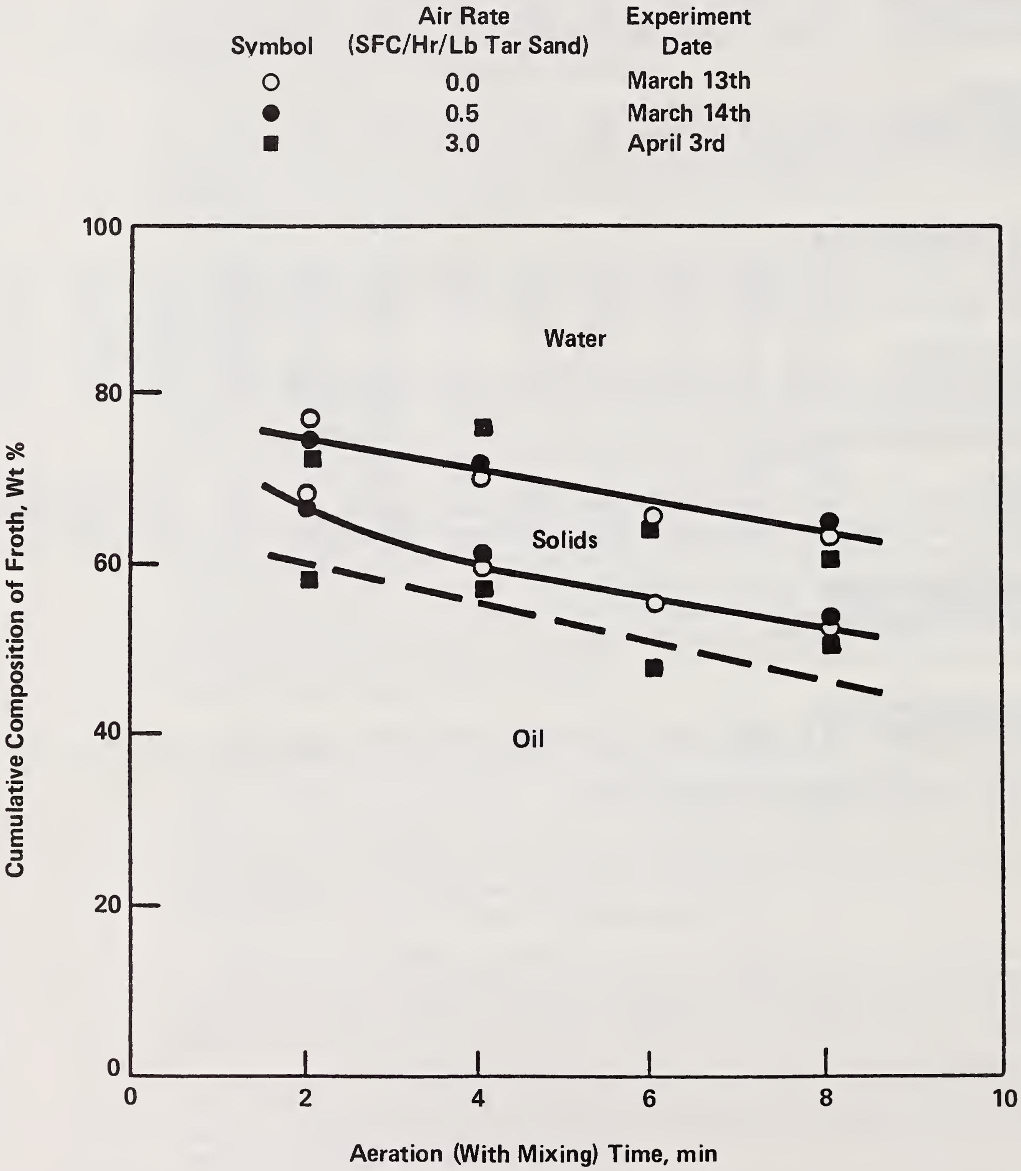


Figure 6-11

Air Rate

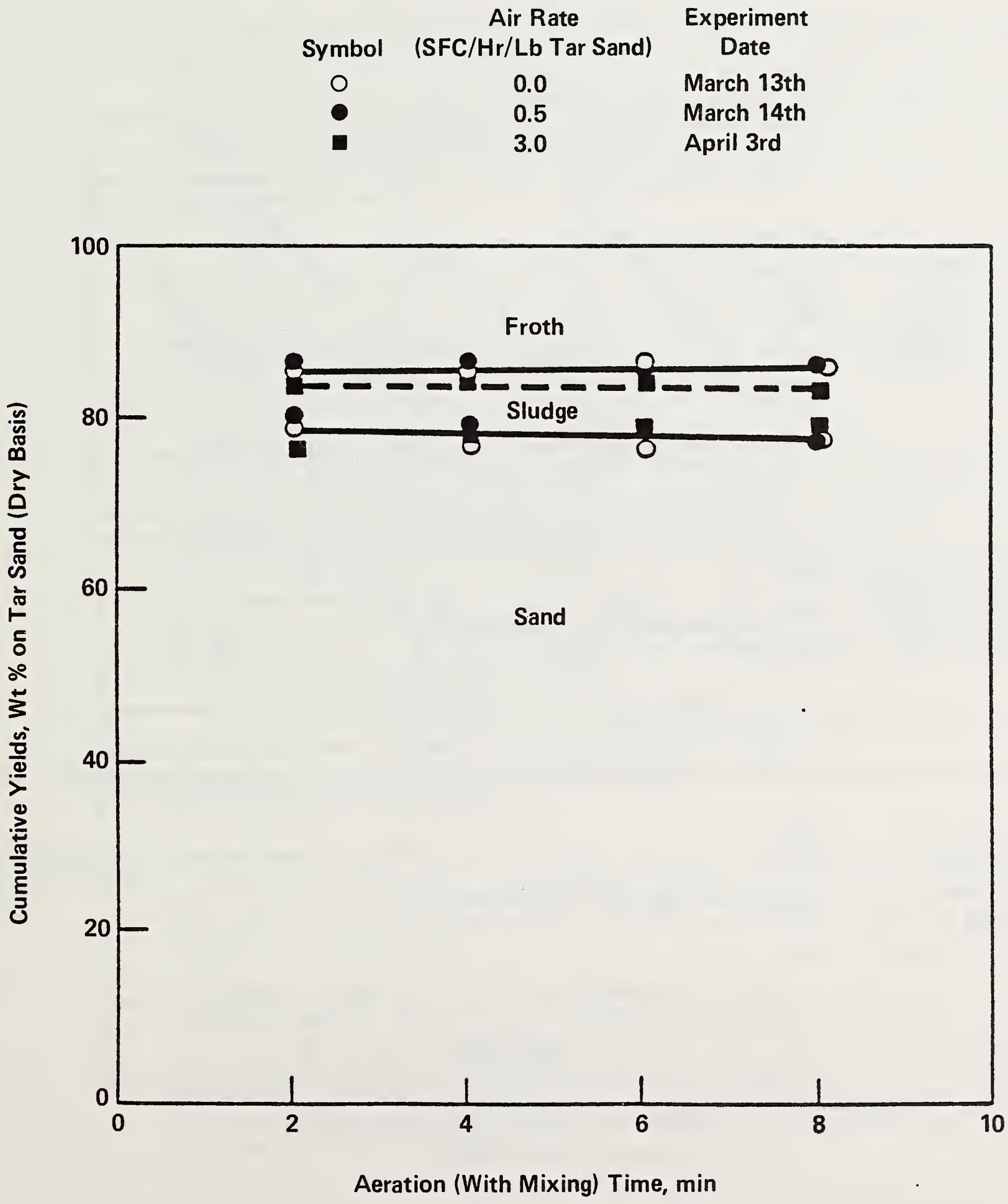
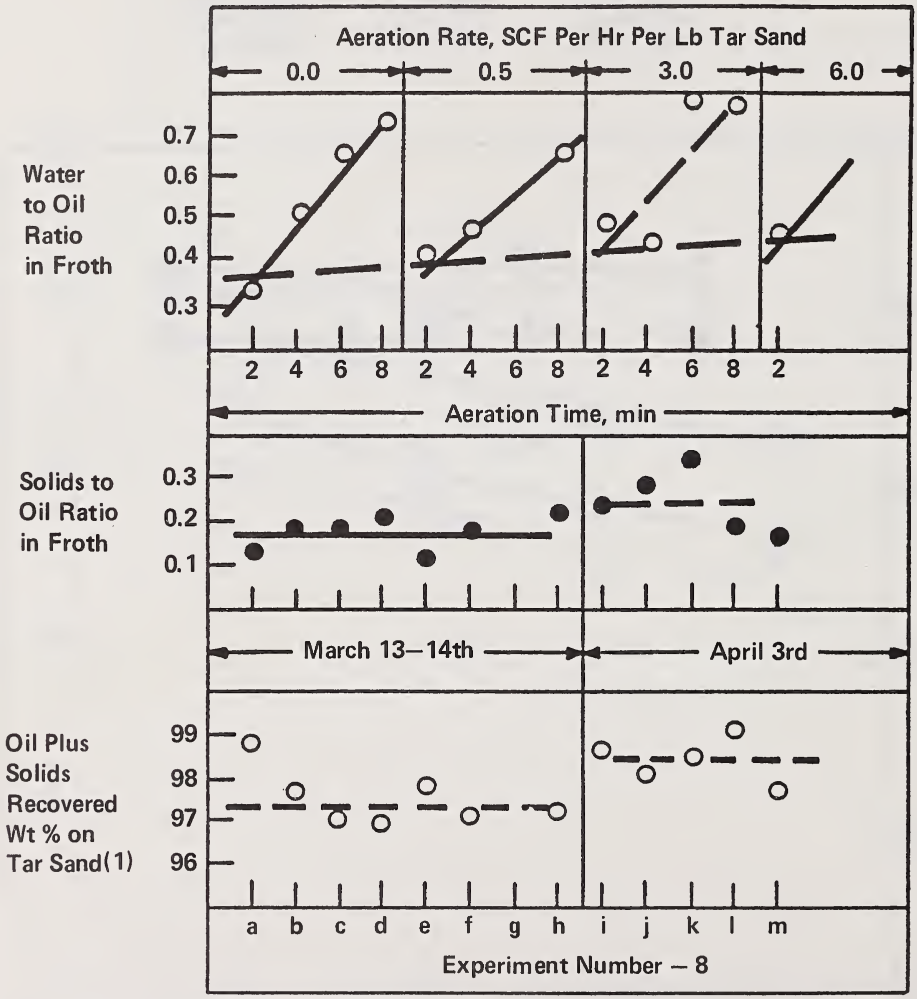


Figure 6-12

Water in Oil Emulsification Increases with Aeration Time : Tar Sand Storage Results in water Loss and Oil-Solid wetting



Note: (1) 100 — Oil plus solids recovered is approximately the water content of the tar sands tion had the same oil content and had similar oil recoveries in separations. It should be noted that the composition of the froth produced from each of these three tar sands was also similar. There are, however, noticeable differences in solids content.

The pH of the water-clay-sludge phase decanted during the laboratory hot water extractions was different in that Area B tar sand appeared to be neutral, whereas Holes 9 and 10 tar sands were acidic.

It was also observed that the ash from this phase appeared to be a mixture of flake-like and powder (amorphous) forms though varied in colour. A mixed straw-yellow and white ash was obtained from experiments with Area B tar sand. While a reddish-brown and white ash mixture was obtained with Area D, Hole 10, tar sand with Area D, Hole 9, an intermediate mixture in colour between these extremes was observed. This indicates iron contamination of at least one component of the suspended solids that is quite common in clay minerals. The wide variation of iron content in the tar sands can also be readily seen by drying, ashing and grinding tar sand samples.

It is possible that the acid behaviour of Area D tar sand and the presence of iron, or other salts, are related. For example, ferric oxide is weakly acidic, and hydrolysis of iron salts such as ferrous carbonate results in weakly acid solutions. This is also true for other carbonates, e.g. calcite. Presumably, the salts (or acids) react with clay and in some way prevent the flotation of fine oil particles through an association mechanism. The oil is lost in the separation stage to the water phase in sludge. The fact that the froth compositions are about the same in this comparison indicates that these salts are associated mainly with the clay in the water phase.

In general terms, the results of the laboratory separations are what might be expected commercially for Area B and Area D (Hole 9) materials, Table 6-18. These tar sands were taken from the formation in block form, and the small samples used in the tests were taken from the centre of the block. The extraction experiments can, therefore, be regarded as being carried out on fresh or undisturbed samples. The laboratory separation conditions were adjusted to simulate what might be a larger scale process. The separation of Area D (Hole 10), however, is better than those reported from the C.S.A. Bench Pilot Unit using a stripper separator. This may reflect the higher oil content of the laboratory sample, i.e. 11.6 wt%; as the Bench Unit indicated a range of oil recoveries from 44.7 wt% (Run No. 1727 C_4) with 8.0 wt% oil in the feed, to 80.4 wt% (Run No. 1828 A_3) with 9.3-11.0 wt% oil in the feed.

The pH parameter was selected for more in depth studies using the semi-mechanized Brass Pot technique of hot water flotation that is discussed in the next section.

B. Pot Experiments

6-11 Water Addition

The amount of water added in mixing was varied from 0 to 30 wt% with a tar sand sample from Area B, that had a high water content of 13 wt%. It was found that froth compositions and oil recoveries did not change significantly within this range of water additions as shown in Table 6-19.

However, separations with a lower connate water content Area B tar sands of about 2.5 wt% showed that slurrying with 10-15 wt% added water is not readily accomplished with mild mixing. This type of tar sand requires that work (shear) be carried out to break open the structure and release water-wet sand, before an homogenous slurry is attained. The minimum amount of water required to effect breakdown of this type of tar sand is related to the oil content. The work required would have to overcome the cohesion of the oil that would be in a more predominate continuous phase at higher oil contents of >10%.

An extension of this would be no separation with very low water content and dried tar sands. In experiments with no aeration and low water addition with an aged Area B tar sand, the water content of the slurry was varied at 11 and 25 wt%. Equivalent results were obtained, Table 6-20, and the expected results were poor.

Table 6-16

Effect of Gas Treatment prior to and during Hot Water Separation (Tar Sand from Area "D" contained 11.1% Water, 9.7% Oil, and 79.2%solids)

Gas Pretreatment of Tar Sand	---	75 hr. under 24 psig ethane at room temp.	16 hr. under 30 psig CO_2 at room temp.	---
Gas Addition in Separation		--------------- Air	----------------	CO_2
Froth Composition, Wt %				
Water	28.2	28.8	28.6	33.8
Solids	14.1	12.9	14.3	13.2
Oil	57.7	58.3	57.1	53.0
Yields, Wt % (water free basis)				
Froth	6.8	6.9	6.5	6.2
Sludge	12.4	12.2	12.8	13.0
Sand	80.8	80.9	80.7	80.8
Oil Recoveries, Wt %				
Froth	49.1	51.5	47.3	46.9
Sludge	39.8	41.1	42.9	44.1
Sand	11.1	7.4	9.8	9.1

Table 6-17

Methane vs. Air as a Flotation Gas (Bad Beaver Creek Tar Sand)

Gas Used in Separation	Air	Methane
Mixing with Gas Addition, Hours	------------------- 35	---------------------
Froth Composition, Wt%		
Water	52	52
Solids	28	37
Oil	20	11
Oil Recovery, Wt%	26	23
pH of Water Phase	7.6	7.7

The amount of water added in mixing was also varied from 15 to 60 wt% with an Area D tar sand. Essentially, no effect was found with additions greater than 20 wt% on slurry, Table 6-21. A slurry was not readily obtained at 16 wt% in mixing and some tar sands still remained "unslurried" after 5 minutes mixing.

With a poor quality Area D Hole 4 tar sand, essentially no effect of water addition in mixing over the range 5-30% was observed on froth quality with or without aeration. However, in these experiments, oil recovery in the froth increased from 45 to 60 wt% with increasing water in mixing when aeration was used.

Three fresh pot samples from Areas B and D (Holes 9 and 11) were separated with both standard 30% water addition and minimum water addition to effect a homogeneous slurry during the mixing stage. The total water for mixing and flooding was maintained the same in all experiments. The results are shown in Table 6-22. It should be noted that no air was used in separation.

In general, it can be seen that there is no advantage for low water additions and in fact, there appears to be an advantage for the standard water addition of <30% in slurrying at which both slightly better froth quality and perhaps higher oil recoveries were obtained with the poorer quality tar sands.

In summary, it has been shown that changes in water addition in mixing over a wide range with Area D and Area B type tar sands do not affect processability significantly except where the water is reduced to a critical condition where slurrying is poor. The amount of water added, however, contributes to the shear in the system that is most important for good slurrying. Hence, it is conceivable that different results might be obtained with different mixing action, such as an intermeshing screw working under pressure and in the presence of air. This has not been explored.

A series of eight spot experiments were carried out to investigate various factors in laboratory separations. In this study, a sample of Area D, Hole 10 was used, and the following discussion is a strict comparison of the results related to the effect of higher total water, Table 6-23. Increasing the total water gave an increase in oil recovery and a very small improvement in froth quality. This may be due to a more dilute dispersion of fine solids in the water phase.

It should be noted that this data does not support the theory of Dr. K.A. Clark, who proposed that a critical amount of water during mixing of 10 wt% was required in order to occlude air into the mixture and hence effect attachment to the oil particles prior to separation by flotation. However, this author supports the concept based on observations that appear to indicate that oil recovery is maximized by the use of an optimum amount of water that presumably will vary with the type of tar sands being separated.

Table 6-18

Comparision of Processability of Tar Sand Samples from Different Locations at Mildred Lake

Tar Sand from Area	B	------ D -------	
Hole No.	-	9	10
Depth, ft.	150	50	5
Oil Content, Wt % of Tar Sand	12.9	11.8	11.6
Froth Composition, Wt %			
Water	30.3	29.6	29.1
Solids	5.1	6.6	8.8
Oil	64.6	63.8	62.1
Solids to Oil Ratio in the Froth	0.79	1.03	1.42
Yields, Wt % (water free basis)			
Froth	14.2	11.7	11.3
Sludge	1.8	3.2	2.4
Sand	84.0	85.1	86.3
Oil Recovery, Wt % in (Output)			
Froth	99.2	87.8	87.4
Sludge	0.8	9.8	10.1
Sand	0.0	2.4	2.5
pH of Water Used	------------------ 8.3 ------------------		
pH of Water-Clay-Sludge Phase	8.3	7.3	6.7

Table 6-19

Effect of Water in Mixing with a High Water area B Tar Sands(Aeration in Separation)*

Water Wt% in Slurry	13	28
Froth Composition, Wt%		
Water	26.9	26.6
Solids	18.6	19.8
Oil	54.5	53.6
Oil Recovery in Froth, Wt%	97.4	95.0

* Complete results are shown in Appendix Table 5.

Table 6-20

Effect of Water in Mixing with an aged Area B Tar Sands

Water Wt% in Slurry	11	25
Froth Composition, Wt%		
Water	31.8	33.1
Solids	26.7	24.2
Oil	41.5	42.7
Oil Recovery in Froth, Wt%	33.3	32.7

Table 6-21

Effect of Water in Mixing with an Area D Tar Sand

Water Wt% in Slurry	16	20	40
Froth Composition, Wt%			
Water	No	53.7	51.1
Solids		19.9	18.6
Oil	Sepn	26.4	30.3
Oil Recovery in Froth, Wt%		87.3	88.1

Table 6-22

Effect of Minimum Slurry and Standard Water in Mixing

Tar Sands	**Area B**		**Area D Hole 9**		**Area D Hole 11**	
Connate Water, Wt%	11.5		3.2		4.0	
Water in Mixing/Flooding	5/75	30/50	15.65	30/50	15.65	30/50
Froth Composition, Wt%						
Water	22.8	22.5	50.0	38.7	86.3	62.1
Solids	10.1	6.7	7.9	4.6	11.2	13.0
Oil	67.1	70.8	42.1	56.7	2.5	24.9
Oil Recovery in Froth, Wt%	99.5	98.7	70.5	74.4	1.8	14.4

Table 6-23

Effect of High Total Water with an Area D Hole 10 Tar Sand

Experiment No.	1	2	3	4
Water in Mixing/Separation	30/50	30/130	30/50	30/130
No. of Aerations	2		1	
Aeration Time, Minutes	5/5		20	
Air Rate, Cubic Ft/Hr	2.0		0.5	
Froth Composition, Wt%				
Water	45.6	43.2	45.8	38.2
Solids	6.1	5.7	5.2	4.9
Oil	48.3	51.1	49.0	56.9
Oil Recovery in Froth, Wt%	78.8	88.2	39.1	48.6

Table 6-24

Effect of Mixing Intensity with an Area B Tar Sand

Mixing Intensity (Stirred Speed) rpm	120	240	240
In Separation: rpm	120	120	240
Froth Composition, Wt%			
Water	26.6	30.9	35.8
Solids	19.7	21.9	20.6
Oil	53.7	47.2	43.6
Oil Recovery in Froth, Wt%	96.1	98.7	99.4
Oil Loss to Sand, Wt%	1.4	0.2	0.06

6-12 Mixing

Increasing the speed of the mixer with a tar sand both in mixing and during aeration, caused an increase in water and solids in the froth, Table 6-24, but an increase in oil recovery and cleaner sand were also obtained.

The same directional changes were obtained with an Area D type tar sand. Further, the mixing intensity effect on solids distribution in the froth for another Area D (Hole 11) sample is shown in Table 6-25. It can be seen that the higher mixing intensity increased the amount of larger sized solids in the froth. This is a result from the action of the impeller that was rotating in the sand phase causing first solution and then dissolution of air. As surfactants adsorbed on the solids act as nuclei for the air coming out of solution, the larger sized solids now with attached air have lower apparent densities and a greater tendency to be carried up to the froth layer. The higher amount of solids below the froth from the higher mixing intensity results in higher entrainment with emulsified water.

Increasing the mixing intensity causes emulsification of more water in the froth at the temperature of separation, i.e. 180°F that is consistent with a low interfacial tension between the oil and the water, that will be discussed in Section 11. Thus increasing mixing intensity increased the water and solids in the froth and also slightly increases oil recovery substantiating previous beaker extraction studies. The higher oil recovery results from the higher shear in mixing that more efficiently separates oil associated with solids. It is obvious that mixing is critical to obtain an optimized result, and will be different for different tar sands.

(a) Effect of Varying Feed Rate

Varying the Area D Hole 10 charge in the technique appeared to effectively change the mixing intensity. The results indicated that froth quality was best with the standard charge of 100 g for which the Brass pot was designed, Table 6-26.

Comparing experiments with 50 and 100 g charges, it can be seen that reducing the charge gave a higher oil recovery, but more solids in the froth. This is a similar result to that found when the intensity of mixing was increased. It can be seen that doubling the charge (100 vs 200 g) resulted in a higher oil content of the sand phase. This is directionally the same as decreasing the mixing intensity. There is an almost drastic reduction in oil recovery. It should be noted that to operate satisfactorily, the flooding water had to be reduced to 65%. This may have had an effect on this result. These data also reinforce the point already made that mixing intensity is a most critical parameter in the hot water flotation process.

(b) Mixing Time

Increasing the mixing time increased the water and solid contents of the froth and also very slightly increased the oil recovery with an Area B tar sand, Table 6-27. This is directionally the same result as that obtained with higher mixing intensities. The effect of mixing time at different mixing intensities on an Area D Hole 11 tar sand can also be seen from the data in Table 6-28.

In this case, the solids in the froth tended to decrease slightly but the oil recoveries increased with increasing mixing time at both low and higher mixing intensities. However, the solids content of the froth and oil recoveries are still significantly higher at the higher mixing intensities.

Comparing the two sets of data in Tables 6-27 and 6-28, it can be seen that longer mixing times with good quality Area B tar sands is detrimental from the point of view of froth quality. Poorer quality Area D type tar sands show a small decrease in the solids in the froth and a small increase in oil content. However, higher oil recoveries are achieved with longer mixing times with both tar sands.

(c) Cold Premixing Tar Sands With Water

During the evaluation of an intermeshing worm mixer for pumping tar sands, the circulating cold slurry of tar sands and water was sampled at different time intervals. Laboratory hot water extractions were carried out on these samples in the brass pot, without the addition of water in mixing. Area D, Holes 9 and 10 tar sands were used in these studies.

Table 6-25

Solids Distribution in Froth

Mixing Intensity (Stirred Speed) rpm	120	240
Solids in Froth Wt% on Tar Sands		
Size: >100 mesh (US Sieve)	0.7 (21)	4.8 (47)
100-200 "	1.0 (29)	2.8 (27)
200-325 "	0.6 (18)	0.9 (9)
325 - "	1.1 (32)	1.8 (17)
Total Solids	**3.4 (100)**	**10.3 (100)**

Table 6-26

Effect of Charge or Mixing Intensity with an Area D Hole 10 tar Sands (2 Aerations of 5 in at 2.0 Cubic ft/hr)

Tar Sand Charge, g	**50**	**100**	**200**
Water in Mixing/Flooding, g	15/25	30/50	60/65
Froth Composition, Wt%			
Water	39.5	45.6	40.3
Solids	14.5	6.1	11.0
Oil	46.0	48.3	48.7
Oil Recovery in Froth, Wt%	84.3	78.8	20.5
Oil Loss to Sand, Wt%	2.0	2.9	43.7

Table 6-27

Effect of Mixing Time with Area B Tar Sand

Time, Minutes	5	10	15
Froth Composition, Wt%			
Water	26.5	29.6	35.8
Solids	19.7	21.6	22.4
Oil	53.7	48.8	41.8
Oil Recovery in Froth, Wt%	96.1	97.8	98.8

The results of these two series of separations are difficult to interpret as the differences found could have resulted from differences in tar sands, sampling, temperature, or equipment configuration. The purpose of mentioning these data, however, is to point out that cold slurrying of tar sand with water for even three hours did not appear to adversely affect froth quality or oil recoveries. In fact, slightly higher oil recoveries are indicated for cold premixing.

In cold slurrying it was observed that a very oily film (~1/8" thick) coated the walls of the return feed pipe early in the operation. An equilibrium appeared to be established in that oil was continually being removed and replaced. It should be noted that another difference was that *three* 90° bends were used in the slurry return line in the first set of experiments, which presented a greater resistance to flow than the 60° angle bends used in the second experiment.

The overall result of prolonged cold mixing, however, appeared to have a beneficial effect on subsequent hot water flotation. This suggests that cold pretreatment of tar sand such as that which might occur in hydraulic transportation would not be expected to have a detrimental effect. Even an advantage may be achieved in the subsequent hot water flotation.

6-13 Aeration Studies

It was shown in the earlier beaker studies, that aeration is a most significant factor in separation. The mechanism of froth formation proposed to explain the improved oil recoveries was that: (a) an oil particle approaches and impinges, perhaps at first by a surface tension effect, on a fresh air-water interface; (b) some oil spreading occurs, although this is not observable with clay particles containing oil and; (c) the particles break through the air-water interface to float on the surface. An air-water interface to improve oil recoveries can either be maintained by progressive or staged skimming of forth and/or by the addition of air to provide internal air-water interfaces which facilitate both the flotation of oil particles and coalescence with bulk froth. These factors will be important in the design of larger continuous separators that will operate with a head of froth under a small hydro station pressure.

This section presents further data on the role of air at different temperatures and with different amounts of water in separation using different quality tar sands in brass pot separations.

(a) Equivalent Air Volume at Different Rates

Spot process studies, have indicated that high air rates for short periods are more effective than low air rates for longer times at equivalent total air volume, Table 6-29. In fact significantly lower oil recovery and a somewhat poorer froth quality were obtained at the longer time and lower air rate. This is consistent with the point of view that froth is a metastable state, that is, once formed it is easily redispersed, and will reform when agitation is stopped.

(b) Effect of Multiple Aerations

If aeration is carried out in stages, a higher oil recovery is obtained, but the froth quality is poorer as illustrated in the following Table 6-30. However, the improvement in oil recovery is probably more significant than the very small degradation in froth quality obtained from consecutive aeration and skimmings.

(c) Effect of Air Rate on Separation Using Different Tar Sands

Studies with different air rates and different tar sands have revealed a family of curves for oil recovery, as shown in Figure 6-13. It is interesting that with no air in separation wide differences in oil recovery are obtained between tar sands. The oil in poor quality tar sands does not float readily. However, with good quality tar sands, high oil recoveries are obtained even with no air in separation. This latter result is similar to those obtained by Clark in hot water separation in pilot plant equipment.

However, it is clearly shown that with a minimum of air in the range of 0.1-0.05 cf/hr as used in the early beaker separation studies, substantial improvements in oil recovery can be obtained with poor quality tar sands. High air rates and two or three aeration-skimmings at rates greater than about one cubic feet per hour gave high oil recoveries with all these tar sands. Air bubble size is also a significant factor as was observed when trying different porosity dispersers when setting up the Pot procedure.

Table 6-28

Effect of Mixing Time with an Area D Hole 11 Tar Sand

Mixing Time, Minutes	5*	15	5	15
Mixing Intensity (Stirred Speed) rpm	----120----		----240----	
Froth Composition, Wt%				
Water	53.2	53.2	54.3	54.0
Solids	19.6	16.8	26.1	24.0
Oil	27.2	30.0	19.6	22.0
Oil Recovery in Froth, Wt%	82.0	89.9	90.9	95.6

* Using average values for results with different amounts of water in mixing for comparison.

Table 6-29

Effect of Aeration Time and Equivalent Air Volume at Different Rates

Aeration Times, Minutes	5	20
Air Rate cu ft/hr	2.0	0.5
Relative Total Air Volume	1	1
Froth Composition, Wt%		
Water	40.9	45.8
Solids	5.6	5.2
Oil	53.5	49.0
Oil Recovery in Froth, Wt%	53.8	39.1

Table 6-30

Effect of One vs. Two Aeratrions

No. of Aerations	1	2
Aeration Time, Minutes	5	5/5
Froth Composition, Wt%		
Water	40.9	45.6
Solids	5.6	6.1
Oil	53.5	48.3
Oil Recovery in Froth, Wt%	53.8	78.8

Table 6-31

Reproducibility and Temperature Studies (Brass Pot) with a Sample (#1) of Homogenized Bench Unit Tar Sands Feed

Tar Sands from Area D, west of Hole 9 was homogenized by C.S.A. for July Bench Unit operations. A spot sample (#1) taken from a portion of this large batch was used in these experiments.(1) The Brass Pot Standard Procedure at three different temperatures was used.

Temperature, °F	150						170						190					
Experiment No. D-32	**1**	**2**	**3**	**4**	**Avg.**	**Std.Dev.**	**5**	**6**	**7**	**8**	**Avg.**	**Std.Dev.**	**9**	**10**	**11**	**12**	**Avg.**	**Std.Dev**
Froth Composition, Wt %																		
Water	45.2	42.7	43.1	43.2	43.53	1.12	47.0	45.5	43.8	45.8	45.56	1.33	45.4	46.4	43.6	45.9	45.35	1.20
Solids	25.1	25.3	26.0	24.2	25.16	0.77	21.6	23.1	24.1	22.2	22.75	1.10	19.8	21.8	24.7	19.4	21.27	2.57
Oil	29.7	32.0	30.9	32.6	31.32	1.29	31.4	31.4	32.1	32.0	31.70	0.39	34.8	31.8	31.7	34.7	33.23	1.76
Wet Froth, Wt %(2) from																		
First Aeration	83.3	77.3	80.8	85.4	81.91	2.80	78.5	75.4	79.5	84.4	79.46	3.71	60.9	69.5	57.5	68.1	63.98	5.76
Second Aeration	16.7	22.7	19.2	14.6	17.92	2.80	21.5	24.6	20.5	15.6	20.54	3.71	39.1	30.5	42.5	31.9	36.02	5.76
Yields, Wt % (water free basis)																		
Froth	16.3	17.1	17.1	16.8	16.84	0.39	15.4	16.4	16.7	16.1	16.14	0.59	14.7	15.5	15.9	15.3	15.33	0.50
Water Phase	4.8	4.2	4.4	4.2	4.40	0.31	5.0	4.5	4.3	4.3	4.54	0.31	5.0	4.8	4.9	4.9	4.91	0.07
Sand	78.9	78.7	78.5	79.8	78.76	0.25	79.6	79.1	79.0	79.6	79.33	0.36	80.3	79.7	79.2	79.8	79.76	0.46
Oil Recovery, Wt % in (output)(3)																		
Froth	92.8	93.3	93.3	94.3	93.42	0.60	93.5	93.9	94.1	94.4	93.96	0.40	91.1	94.0	91.3	93.2	92.45	1.44
Water Phase	4.7	3.8	4.5	3.7	4.17	0.49	4.1	4.3	4.2	4.0	4.15	0.16	6.8	4.2	6.3	4.7	5.47	1.25
Sand	2.5	2.9	2.2	2.0	2.40	0.40	2.4	1.8	1.7	1.6	1.90	0.38	2.1	1.8	2.4	2.1	2.08	0.23
Tar Sand Composition Wt % (cal^c)																		
Oil(4)	9.1	9.9	9.6	9.9	9.66	0.37	9.4	9.8	9.8	9.7	9.68	0.21	10.0	9.4	9.5	9.6	9.62	0.27
Water(5)	4.0	3.2	3.4	3.0	3.39	0.42	3.5	3.0	2.9	3.4	3.21	0.29	2.7	3.2	3.3	2.3	2.89	0.46
Fines(6)	11.4	11.0	11.4	10.6	11.10	0.38	10.5	10.7	10.7	10.2	10.52	0.27	9.4	10.4	10.9	10.2	10.19	0.64
Sand	75.5	75.9	75.6	76.5	75.86	0.42	76.6	76.5	76.6	76.7	76.60	0.12	77.9	77.0	76.4	77.9	77.30	0.77

(1) The 5 lb spot sample (#1) used in these experiments was analysed by Soxhlet Extraction and sieving; and by oven drying and ashing and found to contain 9.6% oil, 3.3% water, 5.8% 325-fines and 81.3% sand.

(2) Wt % on total froth.

(3) Essentially the same as in pot, see note 1.

(4) Grams of oil recovered, Wt %.

(5) 100 - (grams of oil and solids recovered).

(6) Solids recovered in froth and water phase.

The froth quality from these separations appeared to fall into two distinct groups. First, low water-high oil for good quality tar sands. Second, high water-low oil for poorer quality tar sands. However, the solids content appeared to vary significantly in this group. These results are shown in Figure 6-14.

(d) A Linear Plot With Log of Air Rate

The oil recovery and froth quality data shown in Figures 6-15 and 6-16, plot linearly with the log of the air rate over the range of 0.1 to 3.5 cubic feet per hour. The high range being the upper limit of good operation in the brass pot extractions. This relationship appears to be quite fundamental as can be seen from inspection of Figures 6-15 to 6-18.

The oil recovery from one aeration based on the ratio of weights of froth from first and second aerations is also been shown in these plots. These oil recoveries are approximate and low because the froth quality from the first aeration is generally somewhat better in quality than froth from subsequent aerations. They are probably about 80% of the actual oil recovery from the first aeration, based on other data. However, the purpose of showing this approximate data is to indicate that a linear plot is probable, even for a one-stage aeration, and hence will also apply to a multi-staged operation.

It is interesting to note that the slope of the two oil recovery lines for most of the plots is similar. Also, substantial benefits are obtained mostly from multiple skimmings, Figure 6-18, although the latter aeration/skimmings result in decreasing advantages in oil recovery. Clearly there is an economic optimum for this approach to recovery.

(e) Fresh Spot Samples

Three fresh spot tar sand samples of Area B and Area D, Holes 9 and 11, were extracted using 0.0, 0.2 and 2.0 cubic feet per hour of air. It can be seen that the Area B was excellent in quality, in that very high oil recovery and excellent froth quality were obtained with no air in separation. Air degraded froth quality from this tar sand with only a very slight improvement in oil recovery. Area D, Hole 9, tar sand extracted quite well with no air. However, a significant oil recovery improvement was obtained with air additions at only a very small degradation. Area D, Hole 11, tar sand was poor in quality and air was essential to achieve a reasonable oil recovery.

The behaviour shown by these fresh tar sand samples would fit into the series of log plots as shown earlier, and it will be shown that the parameter of the curves in Figure 6-13 is more a function of the "pH" of the tar sands.

6-14 Temperature

An example of the reproducibility of separations at different temperatures with an Area D tar sand is shown in Table 6-31. The tar sand was a spot sample of an homogenized bench unit feed obtained (July 1962) from west of Hole 9. The standard deviations are small, indicating that good reproducibility was achieved. It is surprising that in spite of the manual skimming employed, a high reproducibility in the water content of the froth is obtained. The solids in the froth are high. Only 26 wt% of these solids passed through a 325 mesh sieve. There is only a very slight indication that the solids content of the froth decreases with increasing temperature, which is shown more clearly by the solids to oil ratio in the froths, Table 6-32.

Table 6-32

Solids in Froth Decrease Slightly with Increasing Temperature

Temperature, °F	S/O Ratio in Froth
150	0.76
170	0.72
190	0.64

The greatest variation is in the amount of total froth from the first aeration, although the final oil recoveries are consistent and high. This is also shown in Figure 6-19. There is a slight indication that the oil recoveries tend to decrease at the higher temperature of 190°F.

In general, it may be concluded that there is no significant effect of temperature over the range of 150-190°F. It is interesting to note that the relative density relationship for water and oil is the same over this range, see Section 2.

A high water content, 13 wt%, Area B tar sand was separated at temperatures from 140-190°F, the results are summarized in Figure 6-20. Froth compositions and oil recoveries are similar to the Area D tar sand discussed before. There is little or no effect of temperature on both froth composition and oil recovery over the range of temperature studied. As would be expected from previous work, froth qualities are significantly better than those obtained with an Area D tar sand, compare Figures 6-19 and 6-20, and more oil is recovered particularly in the first aeration.

A sample of tar sands received at Sarnia and designated a new Area 4 tar sand, showed a slight improvement in froth quality with increasing temperature, Figure 6-21. The overall oil recovery, however, was the same at all temperatures, but the oil content of the sand decreases with increasing temperature. Presumably, longer mixing at the lower temperature would have given equivalent results with this type of tar sand.

Eleven experiments were carried out in an effort to define the effect of temperature over the range of 140-200°F, with a sample of tar sand taken from a "bulldozed" cut adjacent to Hole 9. The froth quality showed a fairly consistent pattern with temperature, Figure 6-22, which indicated a slight decrease in solids and increase in water with increasing temperature. The oil recoveries in the froth, however, varied between 77 and 97 wt%. This was thought to be due to variation in feed quality, that had been noticed by a dry appearance in the tar sand homogenizing step.

Hence, a second sample of this type of tar sand was taken, homogenized, and sieved through a 1/4" sieve, which is common practice, and the first pass sieving were collected. The remaining tar sands (40 wt% of the total sample) were rehomogenized and sieved again, and kept separate. These two portions of the total feed were then extracted at 150 and 180 (in duplicate) °F. With the exception of a slightly lower oil recovery at 150°F for the sieved portion of the tar sands, both sets of data show little or no effect of temperature. However, there was a surprising difference in oil recovery between the sieved and unsieved portions with only a very slight difference in tar sand composition. The lumps which were not readily sieved gave an oil recovery of about 72 compared with 97 for the tar sand which readily passed through the sieve. The froth qualities show a fair agreement with those from the total sample. There appears to be a slight decrease in the solids content and increase in the water content with increasing temperature. This is consistent with the initial results on a total sample of this tar sand. The oil recoveries cover the same range as those found experimentally with a total sample. The initial results are, therefore, consistent with the sieved sample being collected progressively in the can.

This example illustrates the need for very careful feed sampling and preparation prior to evaluation. Variation in tar sand feed quality is probably the most significant variable contributing to differences in results from extraction. In this case the poor quality portion of the sample was believed to have occurred through the process of oxidation caused by preworking the area.

An Area D, Hole 11 tar sand showed no effect of temperature over the range of 120-200°F on froth quality and on oil recovery, Figure 6-23. These data were obtained with different tar sand samples and by different operators over a period of three months.

The equivalent results obtained in this temperature range of 120-200°F suggest that flotation is dependent more on the gas content of the oil particles released from the tar sands and occluded in mixing as well as the system used for flotation, than on temperature.

At temperatures lower than 120°F the oil recovery decreased very sharply, Figure 6-23. From the critical temperature - relative density relationship for this type of tar sand, Section 2, a sharp decrease in the ability of the oil from this tar sand to float can be predicted at temperatures lower than 120°F. It is interesting that this transition point coincides with that observed experimentally Figure 6-23. This suggests that only at temperatures less than this critical temperature does the oil gravity play a significant role in flotation. Moreover, it should be noted that the relative density of water and oil could play an important role in flotation even at high temperatures, Section 2.

The fluidity of the bitumen is also important for the froth to reject solids. This can be seen from Figure 6-23 that at temperatures less than 120°F where the solids content of the froth increased markedly, although low oil recoveries were obtained in this region.

In summary, it has been found that tar sands classified as Area B and tar sands from various parts of Area D show no significant effect of temperature on oil recovery in the range of 120-200°F. Higher temperature operations appear to give slightly less solids in the froth, but the water content tends to increase. In general, good oil recoveries are obtained at temperatures above the critical temperature - relative density relationship of water and oil from a given tar sands.

These studies indicate that it may be possible to successfully operate a large scale plant at the lower temperatures of 130-150°F instead of the conventionally accepted 180°F. This is particularly true if froth can be readily upgraded in subsequent processing operations. Satisfactory separation in this lower temperature range has recently been confirmed by CSA Bench Unit Operations.

Figure 6-13

Oil Recovery as a Function of Air Rate for Tar Sands of Different Quality

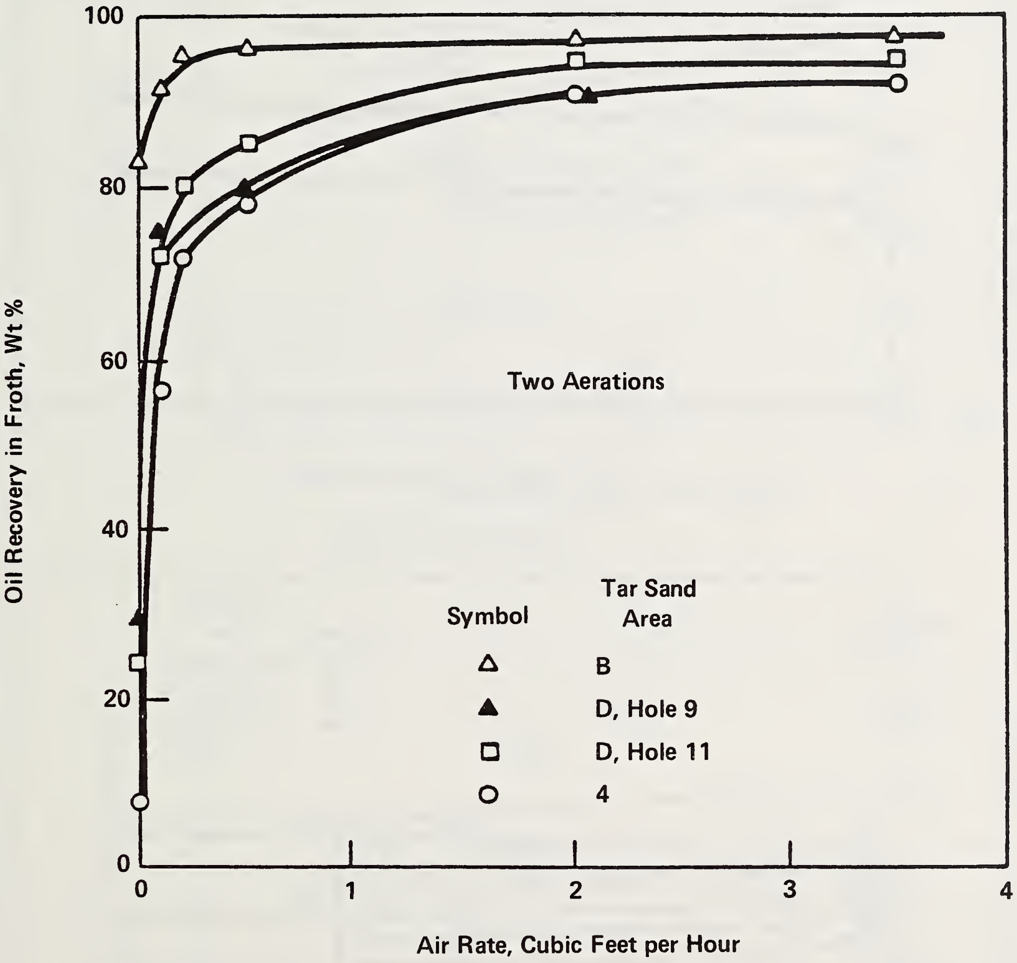


Figure 6-14

Froth Composition as a Function of Air Rate for Tar Sands of Different Quality

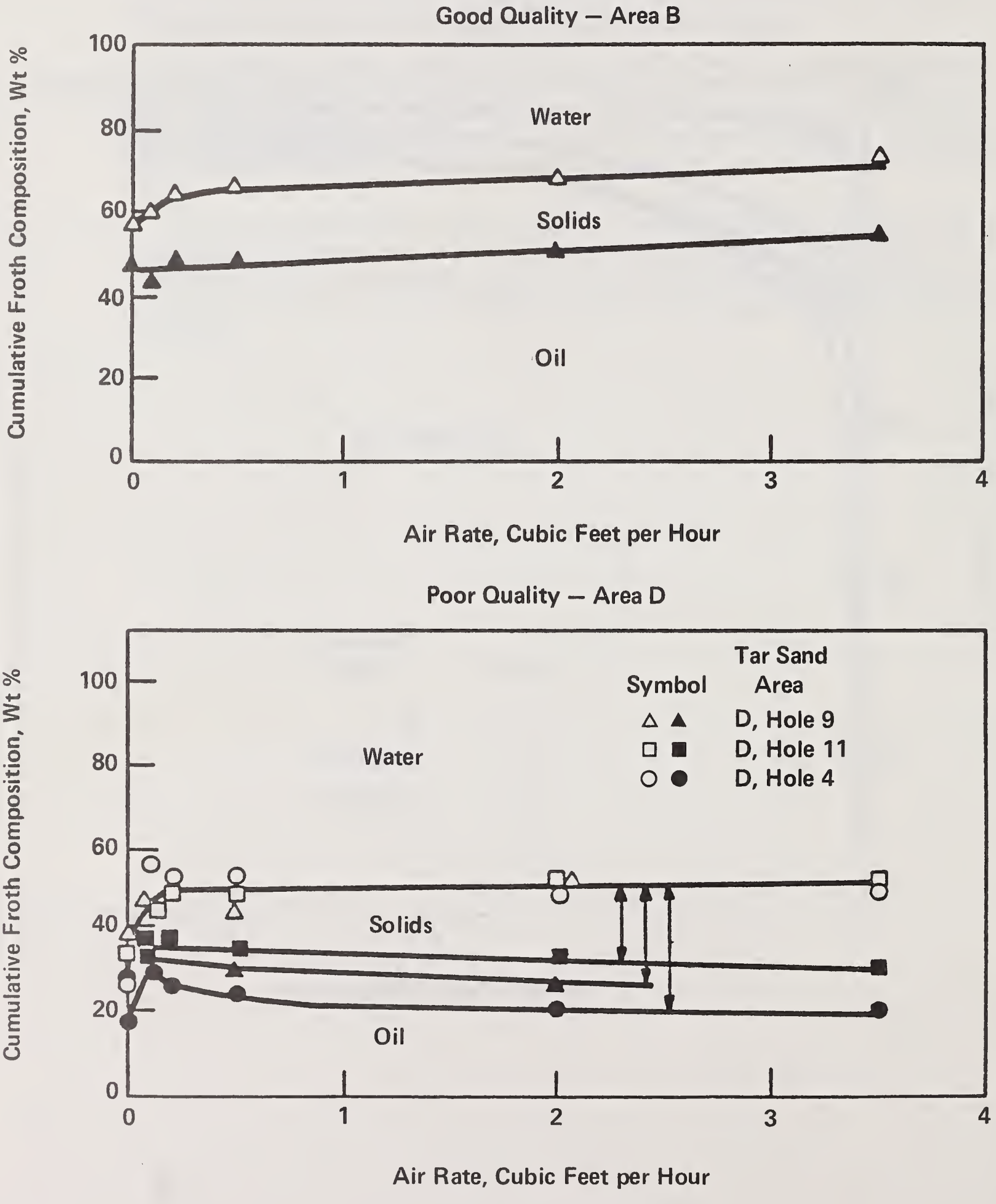


Figure 6-15

Good Quality Tar Sands - Area B - Gave High Oil Recoveries and Good Froth Qualities, Linear with Air Rate in the Range 0.1-3.5 cubic Feet/Hour

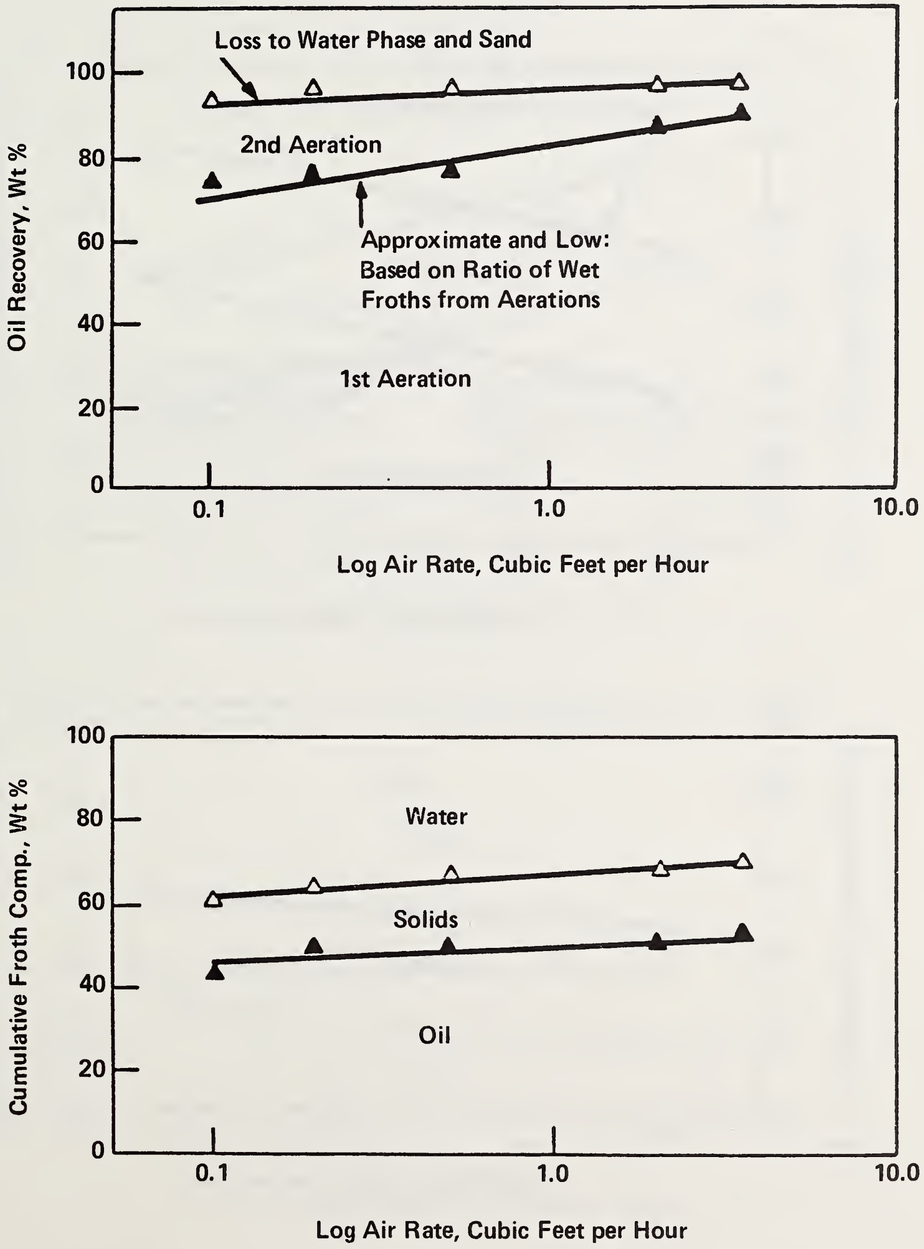


Figure 6-16

Progressive Aeration Is Most Significant for High Oil Recoveries with Poor Quality Tar Sands - Area D, Hole 11 : Higher Air Rates Increased the Solids Content of the Froth

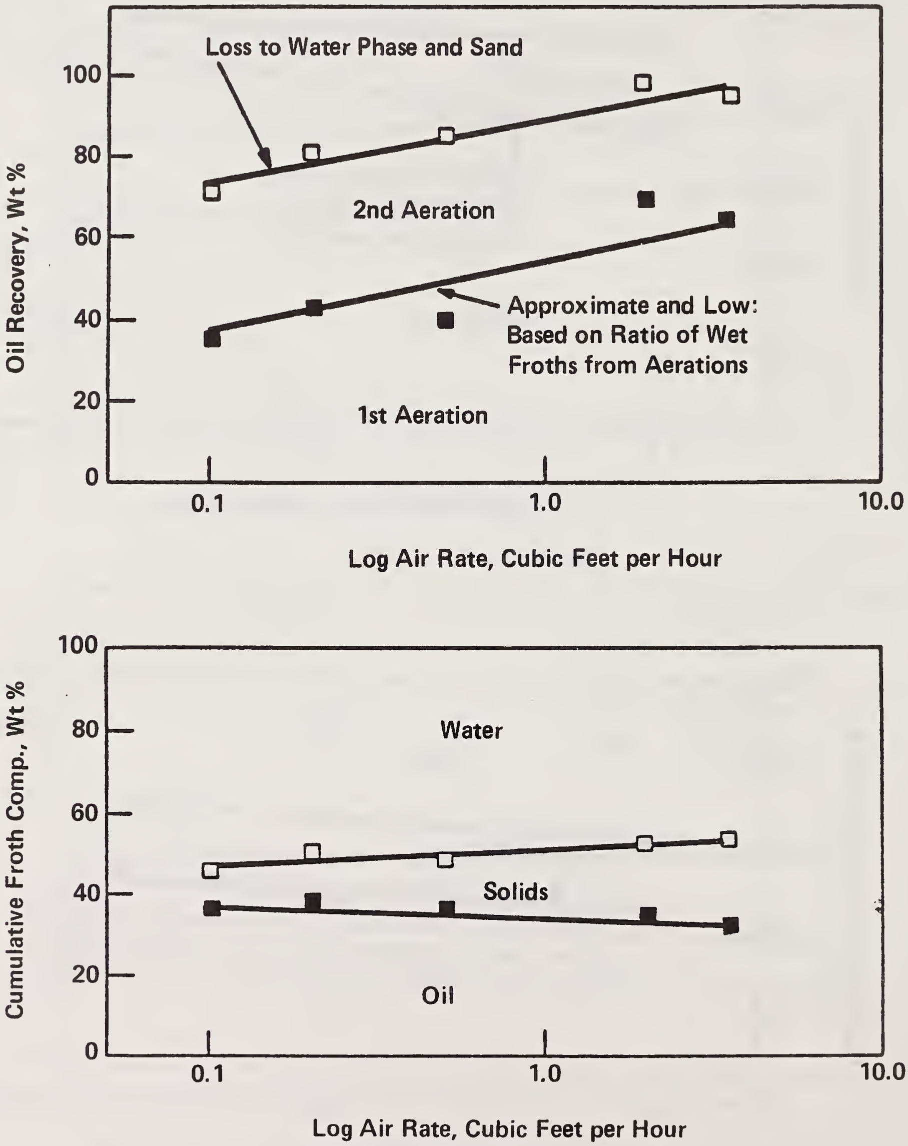
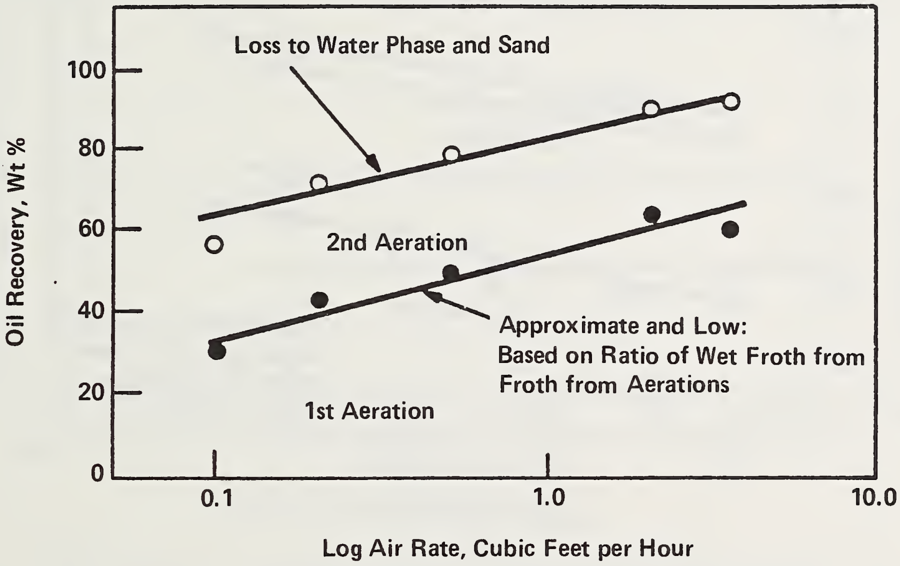


Figure 6-17

Higher Air Rates and Progressive Aerations Gave High Oil Recoveries, but Poor Froth Quality with a Poor Quality Tar Sand - Area 4



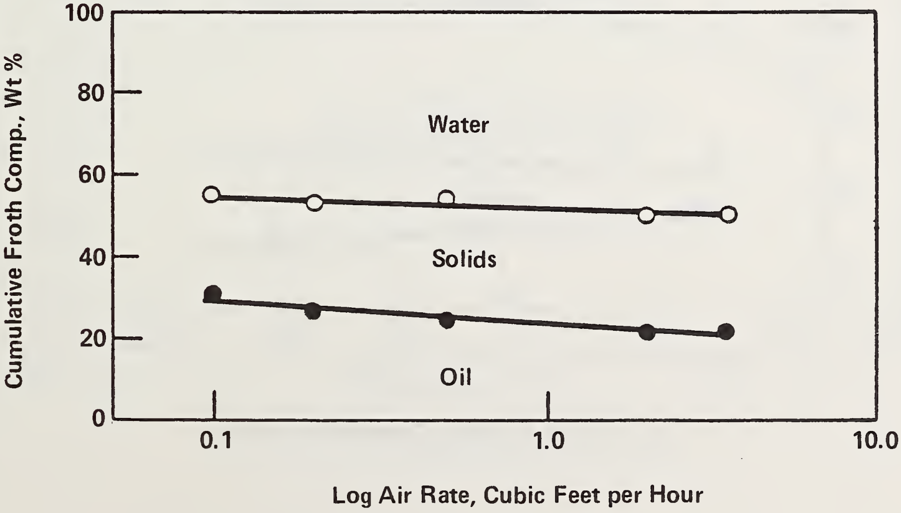


Figure 6-18

Progressive Aeration Gave Higher Oil Recoveries with a Poor Quality Area D (Hole 9)

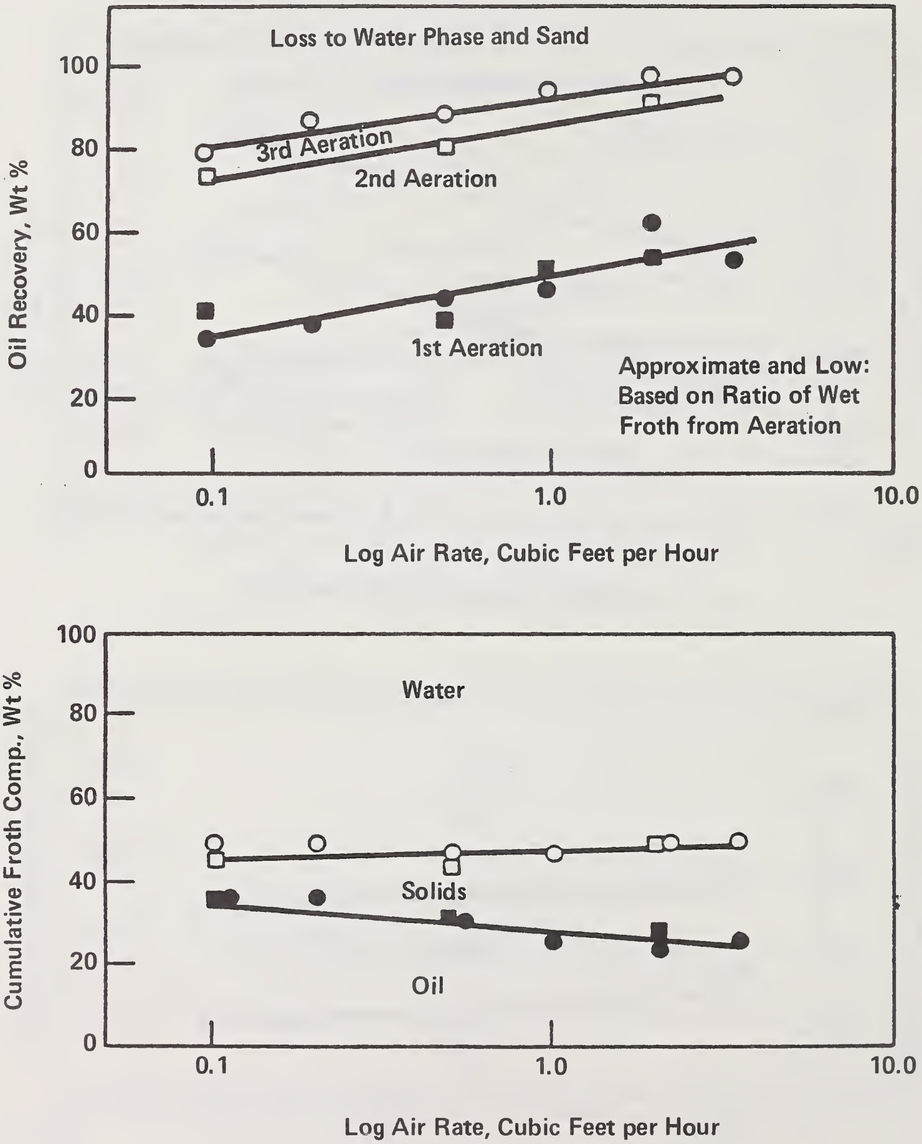
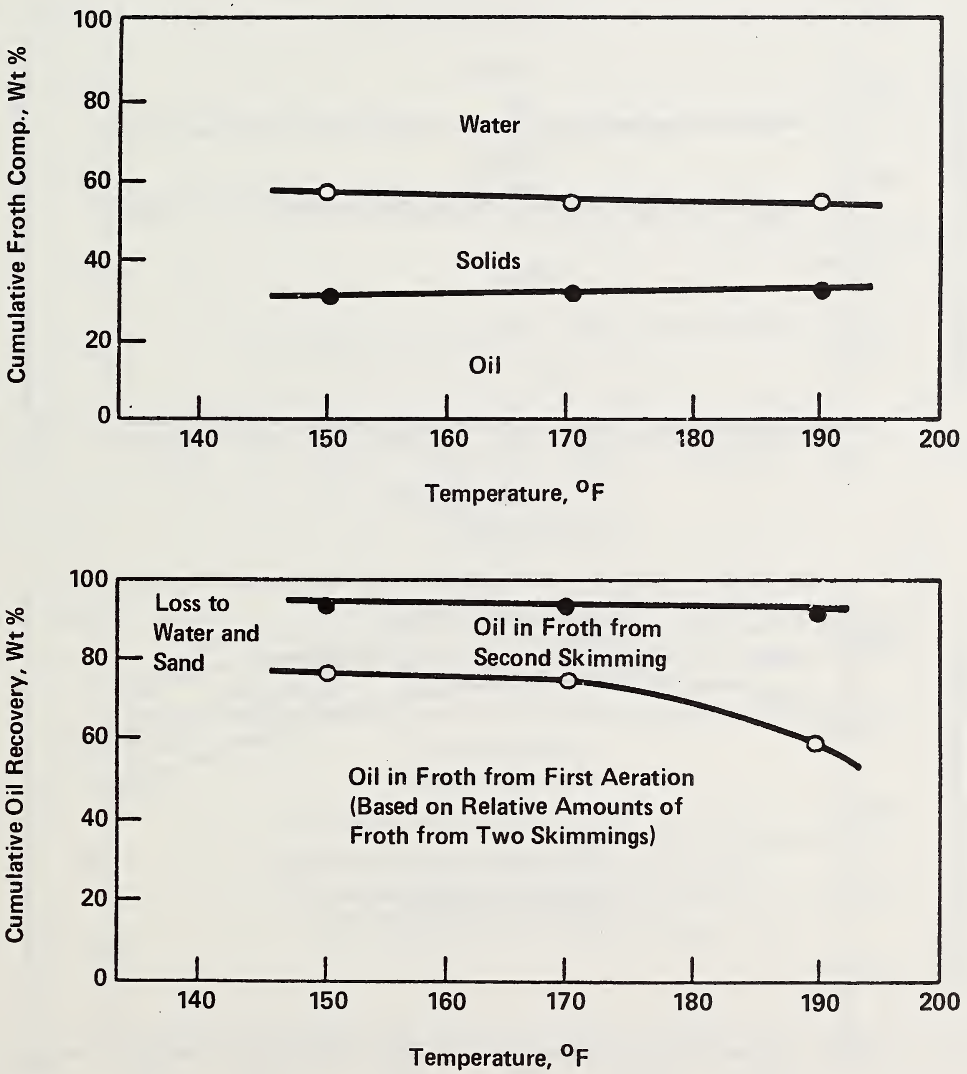


Figure 6-19

Effect of Temperature on Froth Composition and Oil Recovery with an Area D (West of Hole 9) Tar Sand

(Averages of 4 Data Points)



(Constant in Mixing—Aeration—Skimming)

Figure 6-20

Effect of Temperature on Froth Composition and Oil Recovery with a High Water Area B Tar Sand

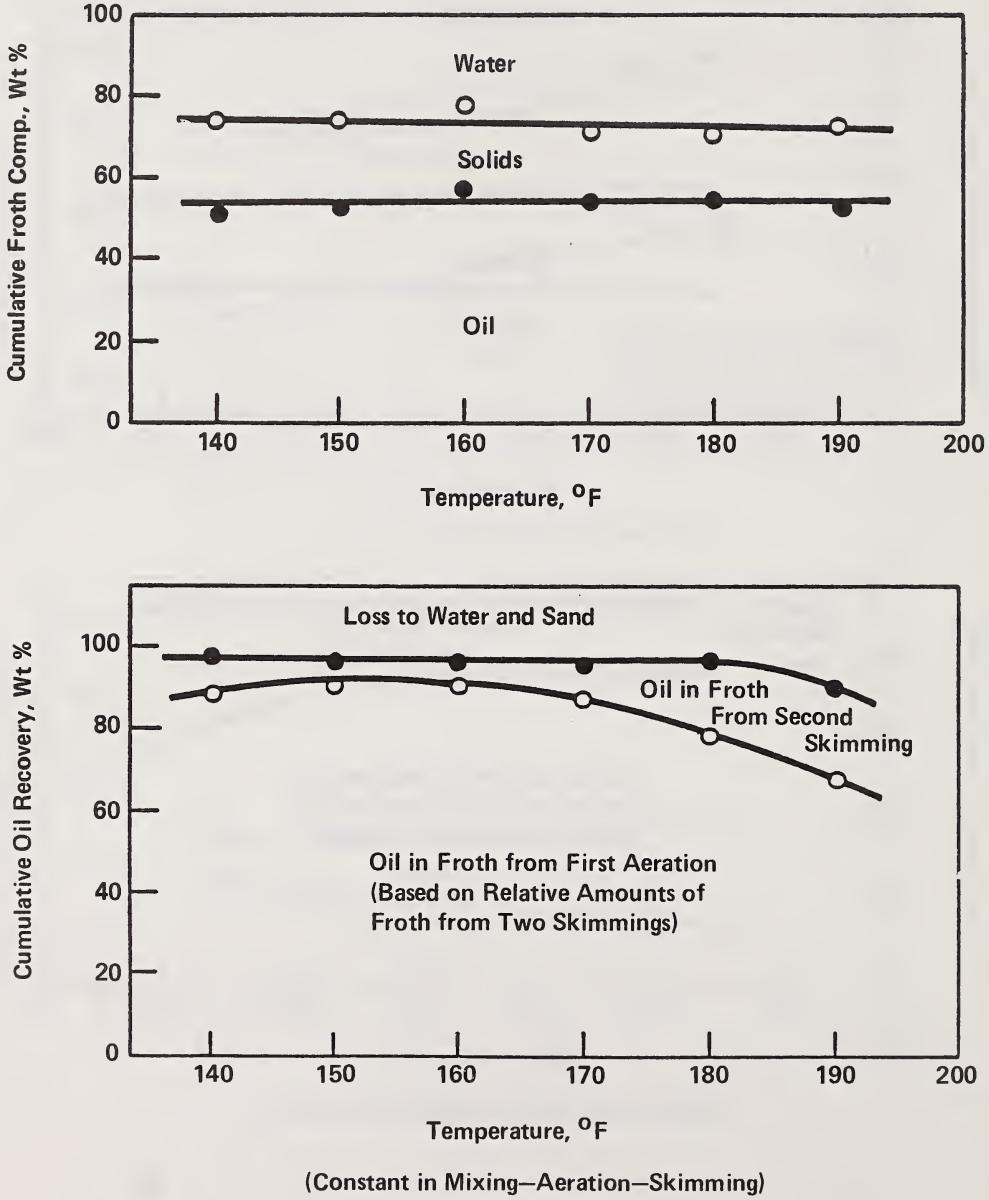
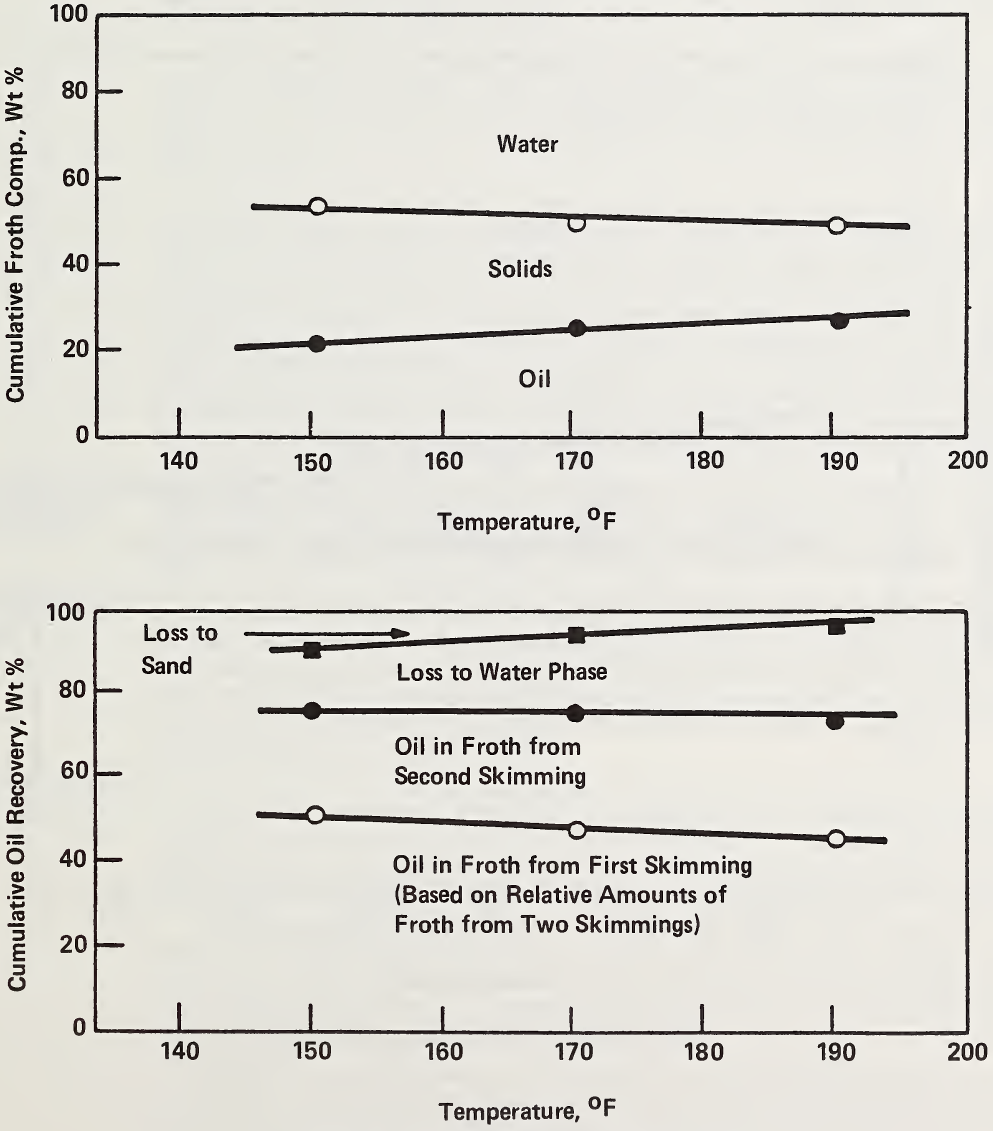


Figure 6-21

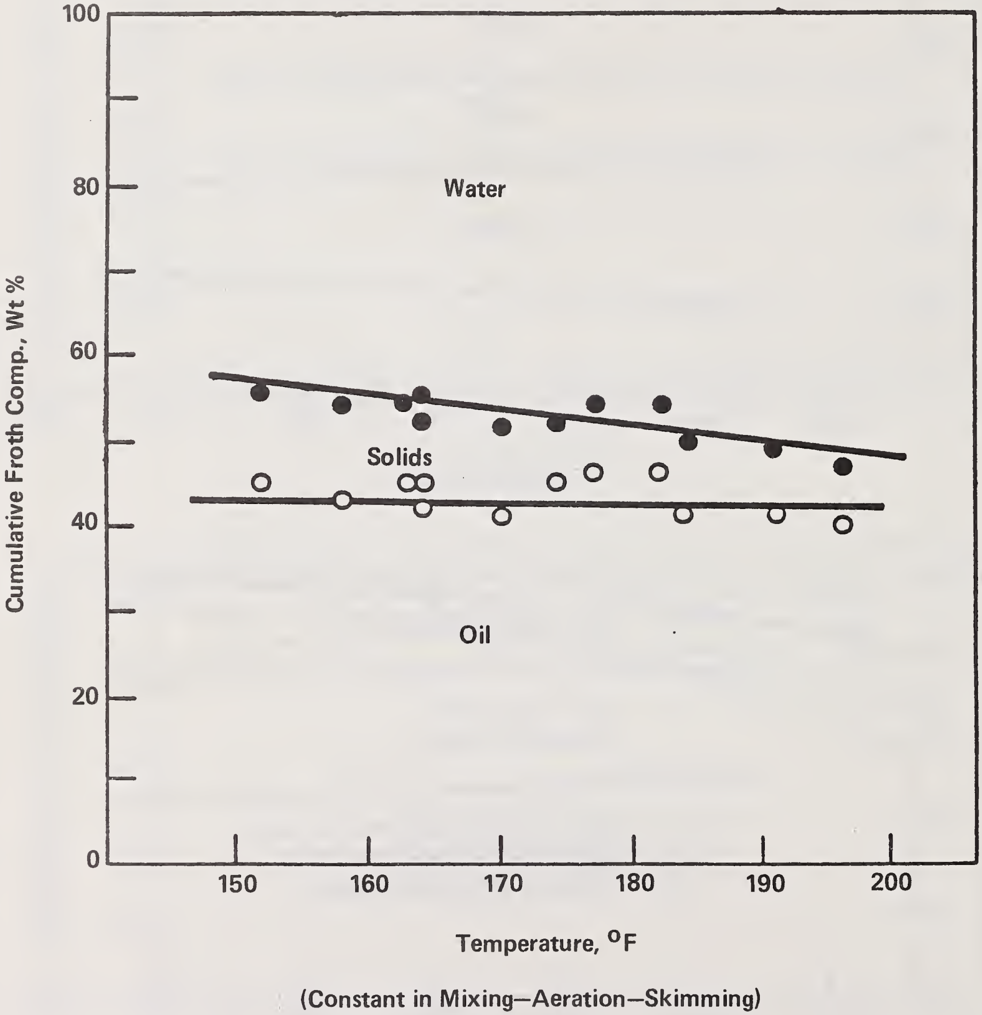
Effect of Temperature on Froth Composition and Oil Recovery with an Area 4 Tar Sand



(Constant in Mixing—Aeration—Skimming)

Figure 6-22

Effect of Temperature on Froth Composition and Oil Recovery with an Area D Tar Sands from Cut Adjacent to Hole 9



6-15 pH Effect

There are several factors that affect processability. The primary factors have been found to be oil and fines in the tar sands, and pH. Other factors that may also correlate with processability, are at present considered to be dependent on these primary factors, and especially pH.

Some studies of the effect of pH in beaker experiments were discussed in Section A. These studies showed that the water phase from separations with Area D tar sand was acidic and poor processability results were obtained; whereas, neutral to alkaline tar sands (Area B) demonstrated good processability. As freshly dug oil sands are slightly alkaline, high oil recoveries are achieved with these samples.

Although a general classification of processability by Areas is used for convenience in discussion, it appeared from these studies that classification of sample processability by pH measurements was also valid. Routine pH measurements on the water phases were, therefore, adopted in laboratory separations. Sample designation by Area and core hole number, however, is still maintained.

Average processability results at standard conditions, tar sand analyses and pH measurements from unrelated studies on process variables with different tar sands are plotted in Figures 6-24 and 6-25 against pH. The upper curve as defined by (open points) shows a well-defined relationship. The lower curve (closed points) is approximate, as it is based on the ratio of the weights of wet froth from two consecutive aerations and does not allow for differences in froth quality that occur between first and second aeration. An estimated corrected line for this effect is also shown. The scatter in the data is mainly attributed to the inaccuracy in pH measurements, as the meter used was subject to fluctuations and was later replaced. Froth quality is also in general related to the pH of the tar sands, Figure 6-25. It should be noted that no caustic addition was used in these experiments. The effect of caustic will be described in the next section.

6-16 Effect of Oil Content

In general, Area B contains more oil and less fines of clay minerals than Area D tar sands, and separations are poorer with these latter tar sands. The oil content of tar sands is clearly a parameter, as was shown before, Figure 6-26, and will be shown again in the next Section C.

6-17 Effect of Fines

Froth quality although related to the "naturally occurring pH", of the tar sands shows a good correlation with fines (325-mesh) content of Area D type tar sands, and hence the concentration of the fines in the water phase. The effect of 325-fines on froth quality is shown in Figure 6-26. As the amount of fines in the tar sand increases, both the solids and the water in the froth increase, and the oil decreases correspondingly. This can have a significant effect on subsequent contaminants removal by Solvent Dilution.

6-18 Iron Content

Processability results on 12 characterization samples are shown in Table 6-33. As pointed out in Section A, the correction factors used in calculating oil recoveries were based on the ash distribution values of the individual solids, hence the oil recoveries shown are more absolute. These tests were carried out in duplicate. The results agreed within 1.2% for all determinations.

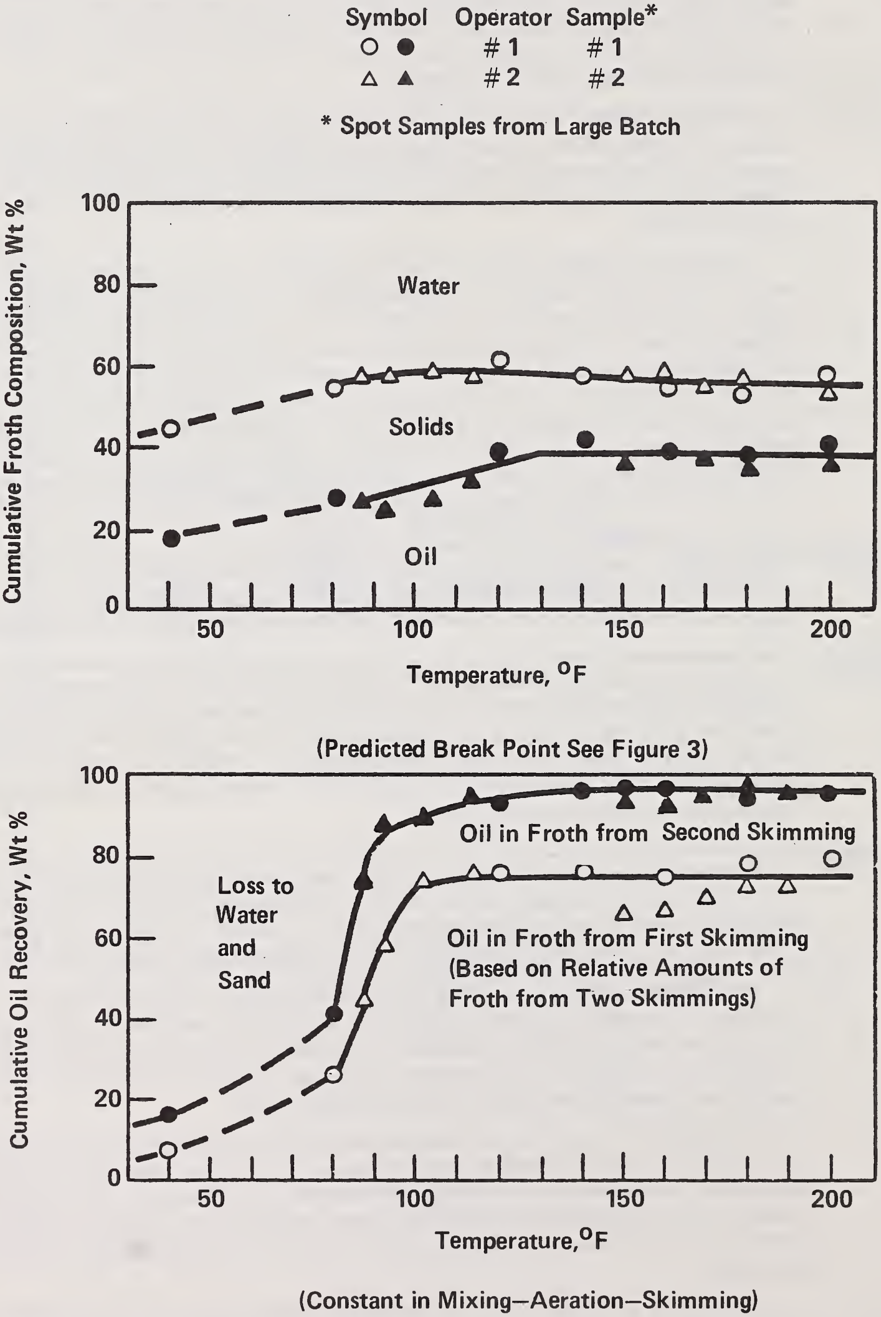
Iron determinations on the solids from the froth water phase were obtained by X-ray fluorescence calibrated by chemical analyses on some standard samples. No correlation of total iron with processability can be seen. However, the relative amounts of iron in the froth did show a very rough correlation with oil recovery. This may only reflect pH in that soluble iron is precipitated as hydroxide and is collected in the froth.

In Figure 6-27, the oil recovery has been plotted as a function of the wt% ash of the sand. Two-thirds of the data indicate that a relationship exists between the sand state and the degree of oil recovery. As pointed out in Section C, the sand ash can be reduced by the presence of heavy minerals, carbon fragments and hydroxyl groups associated with solids or minerals. Three points, however, fall outside of this correlation. These three tar sands exhibited either low pH or high fines.

Also shown in Figure 6-27 is a relationship between oil recovery in the froth and the weight % fines on tar sands. Again a general relationship exists for most of the data, although it

Figure 6-23

Effect of Temperature on Froth Composition and Oil Recovery with Area D, Hole 11 Tar Sand



should be noted that 325- and oil contents are also related, Section III. The two exceptions in the correlation exhibit low pH. These relationships indicate that processability may be related to the state of the solids.

6-19 Pilot Comparison

The Sarnia oil recovery and froth quality results are compared with those obtained in CSA Mildred Lake Bench Unit and laboratory separations on the same grades of tar sands, Figure 6-28. The oil recovery shows a very good correlation for high oil content tar sands. However, there is considerable scatter for lower oil content tar sands. Obviously, other parameters such as pH and the degree of clay contamination with metal ions, e.g. Fe, are also parameters of sorts.

It is interesting that the plot of the cumulative froth composition shows a similar relationship with the CSA Laboratory data . The Bench Unit froth composition had a higher water content of about 14% and slightly less solids. The shape of the curves for all three studies are similar that indicates there is a correlation between the Bench Unit and the laboratory results. The higher water and slightly less solids achieved in the Bench Unit could result from higher mixing intensities. It should be noted that three aeration skimmings were used in the bench unit operation, compared to two in the laboratory standard separation.

6-20 Summary

Processability has been found to be related to the oil content of the tar sands and the amount of fines. pH is an important factor in flotation that has long been acknowledged. However, the theory lags behind the practice. These studies show that oil recovery in hot water flotation is a function of the "naturally occurring pH" of the tar sands, with neutral to alkaline tar sands giving high oil recovery, and neutral to acidic tar sands giving poorer oil recovery and somewhat poorer froth quality. Other secondary factors such as the state of the time solids and metals (which would include heavy minerals and carbonaceous fragments) will correlate to some extent, as they are probably interrelated to some extent with the three primary factors. A clearer definition of effects of these secondary factors is required on a variety of oil sands in order to be able to predict performance.

C. Process Control Evaluation

6-21 Oil Sands Classification

Classification, by history and composition of the eight tar sands that were used in these studies on process control, are summarized in Table 6-34. Differences in pH, conductance, zeta potential and soluble salt or ionic strength, as possible processability parameters, were also measured, Table 3-35. Processability using standard separation conditions are summarized in Table 6-36.

6-22 Process Energy Input

To study the basic parameters in flotation, a method to simulate at least oil recovery presently obtained in the Syncrude pilot plant was required. The Brass Pot was readily modified by reducing the total input agitation energy. This was accomplished in a three stage operation. In the first stage no air was added to the Pot. This was followed by two aerations simulating secondary and tertiary oil recoveries in second and third froths, respectively. The basic problem was one of what level of agitation to use.

The elimination of air in the first froth separation and collection, greatly reduced the agitation energy input. Hence, the mixing speed in the separator was evaluated Table 6-37. An almost optimum speed at 800 rpm was obtained, where oil recovery without aeration in primary separation was a maximum of ~89%. This is approximately equivalent to that obtained in the Syncrude Pilot Unit. This data is plotted in Figure 6-29.

In contrast to the no aeration froth operation shown in Figure 6-29, the effect of increased mixing speed with effective aeration is small. The oil recovery is high and appears to increase very slightly. This data again supports the concept that optimized conditions in primary separation is the route to take, using aeration only in secondary oil recovery. Further, this optimum separation could be attained in any suitably designed separation by adjusting the agitation energy input.

Figure 6-24

Processability Is a Function of pH of Tar Sands

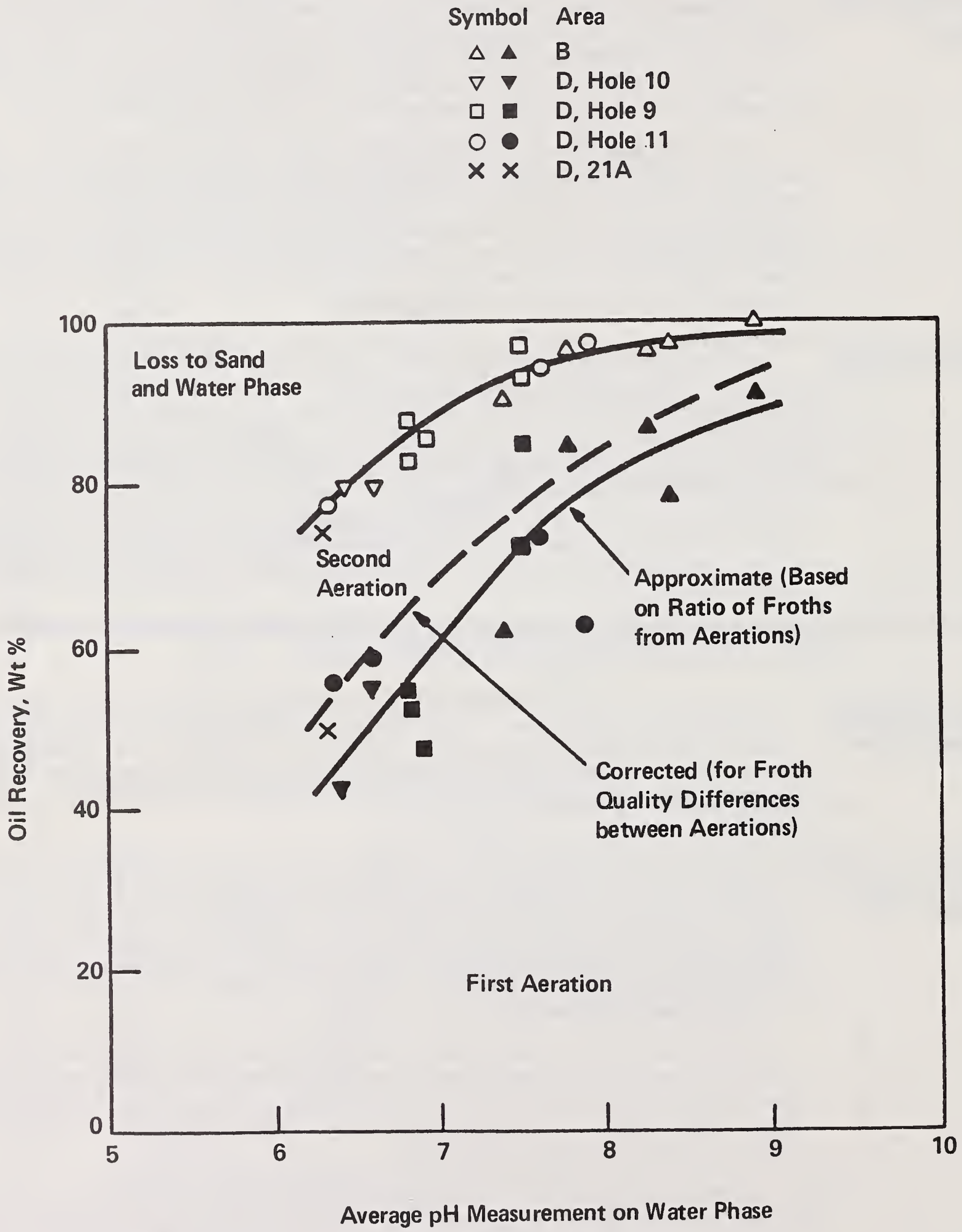


Figure 6-25

Froth Composition Is Related to pH of the Tar Sands

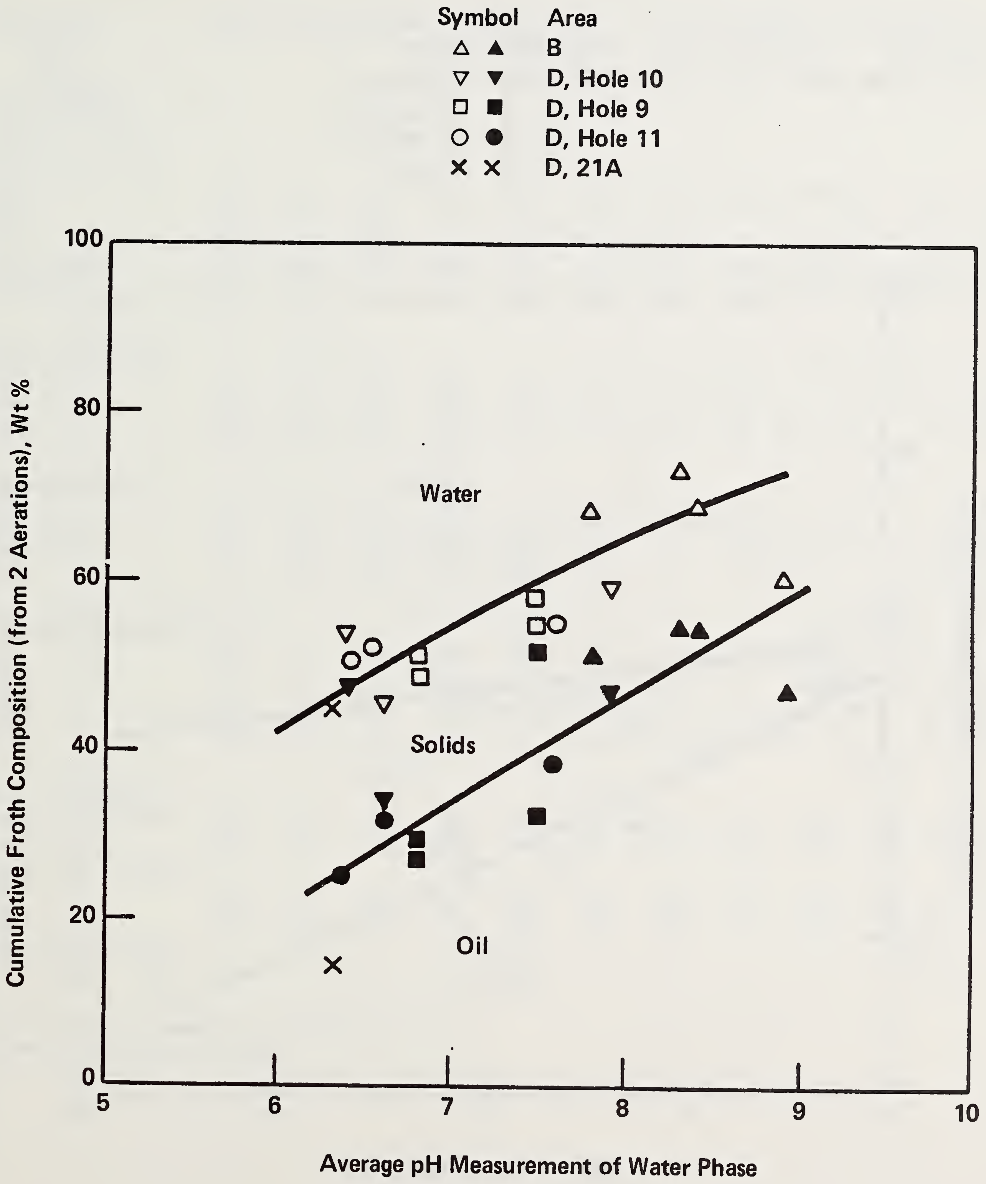


Figure 6-26

Fines in Area D Feeds Have a Significant Effect on Froth Quality

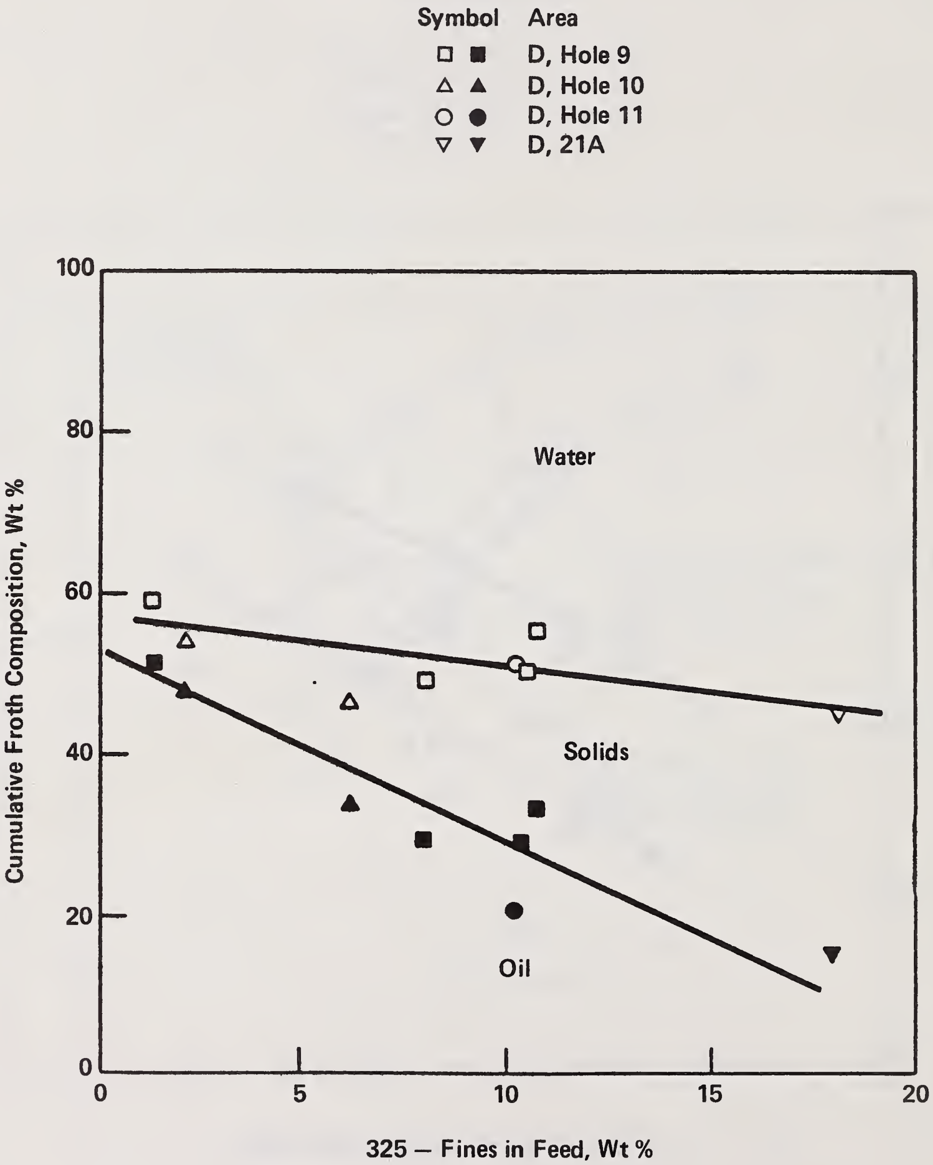


Table 6-33

Hot Water Flotation Separations (Brass Pot) of Tar Sand Characterization Samples at Standard Conditions

Core Number	Area B	Hole 11	Hole 21A	15-16-2			29-16-2			33-14-2		
Depth	-	-	-	Top	Middle	Bottom	Top	Middle	Bottom	Top	Middle	Bottom
Footage	-	-	-	67-99	115-163	163-214	32-63	63-110	110-174	79-110	110-159	174-206
Processability Results(1), Wt %												
Froth Composition												
Water	33.0	47.1	57.0	58.3	42.8	40.1	38.5	44.8	35.5	36.9	39.6	36.7
Solids	14.1	33.2	23.2	23.7	25.7	23.2	13.4	15.3	10.0	19.9	22.7	20.9
Oil	52.9	19.6	19.8	17.9	31.6	36.6	48.0	39.9	54.5	43.2	37.7	542.5
Water/Oil Ratio	0.62	2.40	2.88	3.26	1.35	1.10	0.80	1.12	0.65	0.85	1.05	0.86
Solids/Oil Ratio	0.27	1.69	1.17	1.32	0.81	0.63	0.28	0.38	0.18	0.46	0.60	0.49
Yields (Dry Basis)												
Froth	17.1	11.3	17.3	6.8	7.9	14.3	15.4	15.7	13.1	13.3	14.2	15.8
Water Phase	2.9	3.5	9.7	16.8	29.4	14.3	4.1	8.4	3.5	8.5	15.6	11.7
Sand	80.0	85.2	73.0	76.4	62.7	71.4	80.5	75.8	83.4	78.1	70.2	72.5
Oil Recoveries in												
Froth	97.9	48.8	82.0	48.9	61.0	90.4	96.6	95.6	97.0	91.4	91.9	94.3
Water Phase	2.1	9.0	11.1	39.0	26.0	9.2	2.1	2.8	2.3	7.1	7.9	5.1
Sand	0.1	42.2	6.9	12.1	13.0	0.4	1.3	1.7	0.7	1.6	0.3	0.6
Tar Sand Composition (Cal^c)												
Oil	13.2	8.1	8.6	5.5	6.7	9.2	12.0	11.3	10.9	9.4	8.7	10.5
Water	4.3	6.1	11.2	8.5	7.1	5.2	3.5	5.1	4.9	5.3	9.8	6.7
Fines	5.9	9.2	16.0	16.8	28.9	18.0	6.9	11.8	5.0	11.4	18.2	15.3
Sand	76.6	76.6	64.2	69.2	57.3	67.6	77.5	71.8	79.2	73.9	63.3	67.6
Iron(2), Content of												
Froth: On Ashed Solids	6.85	1.29	2.57	2.59	4.86	3.62	3.77	5.50	4.39	2.76	5.06	4.86
: On Tar Sands	0.21	0.07	0.20	0.08	0.14	0.17	0.11	0.23	0.08	0.10	0.20	0.18
Water Phase: On Ashed Solids	1.91	1.59	1.76	1.62	2.52	1.92	2.69	3.07	1.98	1.50	3.77	3.84
: On Tar Sands	0.04	0.04	0.13	0.20	0.59	0.22	0.09	0.21	0.05	0.05	0.46	0.38
Sand: On Ashed Solids	-	-	-	-	0.45	-	-	-	-	-	0.18	-
: On Tar Sands	-	-	-	-	0.26	-	-	-	-	-	0.12	-

(1) pH readings were not obtained due to instrument failure.
(2) Measured by X-ray fluorescence analysis.

Table 6-34

Classification of Type and General Inspections on Beaver River Tar Sands used in Studies

Arbitrary Oil Sand Grouping	A	B				C		
Time Description	Old-Aged					New-Fresh		
Date Received, Sarnia	Nov 1964	1964			Nov 1964	Feb 1966		
Designation	Plant Feed	Good	Intermediate	Bad	Bench No. 1	Unit Feeds - Run No. 6	7	9
Sample Location	"Composite"	Representative of Types Used in Blend of Composite			Upper Few Feet of Deposit	Cut from Bench No. 3 Sept '65(1)	Nov '65(2)	30' South of Core Hole #1
Storage (Months) Prior to Shipping to Sarnia	Cold (?)				None	In Root Cellar on Escarpment	Lab M.L.	None
Composition, Wt% on Tar Sand								
Water	4.0	2.0	2.3	3.7	3.4	4.9	3.0	4.5
Solids	85.0	87.1	88.2	89.9	85.6	85.5	87.4	86.0
Oil	11.0	10.9	9.5	6.4	11.0	9.6	9.6	9.5
Clay (325+)	16.3	21.2	17.1	18.8	12.0	11.0	15.1	14.3
Heavy Minerals (325+)	0.37	0.44	0.59	0.40	0.58	0.52	0.55	1.44

(1) Bench No. 3 tar sand stock piled (open to atmosphere) for several weeks before roughly homogenizing with mined Bench No. 5

(2) Freshly exposed cut.

Figure 6-27

Effect of Sand State and Amount of Fines on Oil Recovery

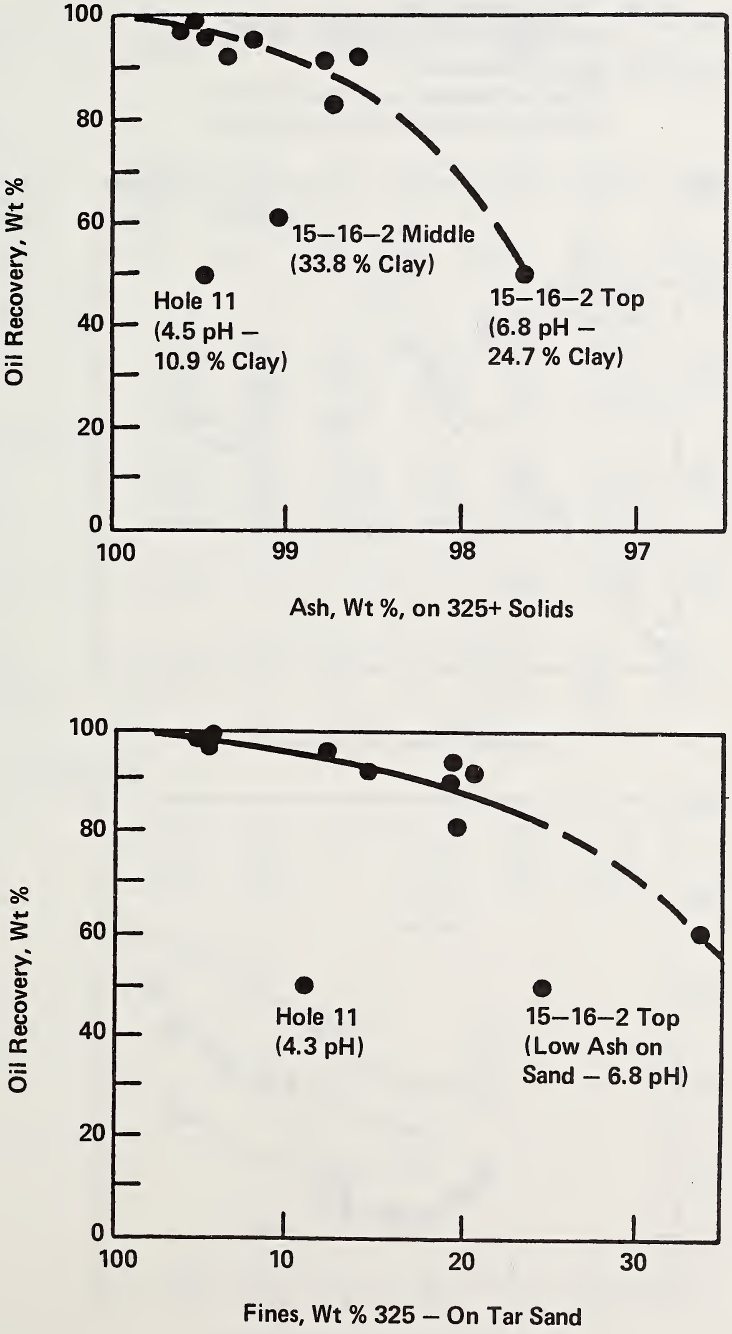


Figure 6-28

Preliminary Comparison of Hot Water Flotation Separations

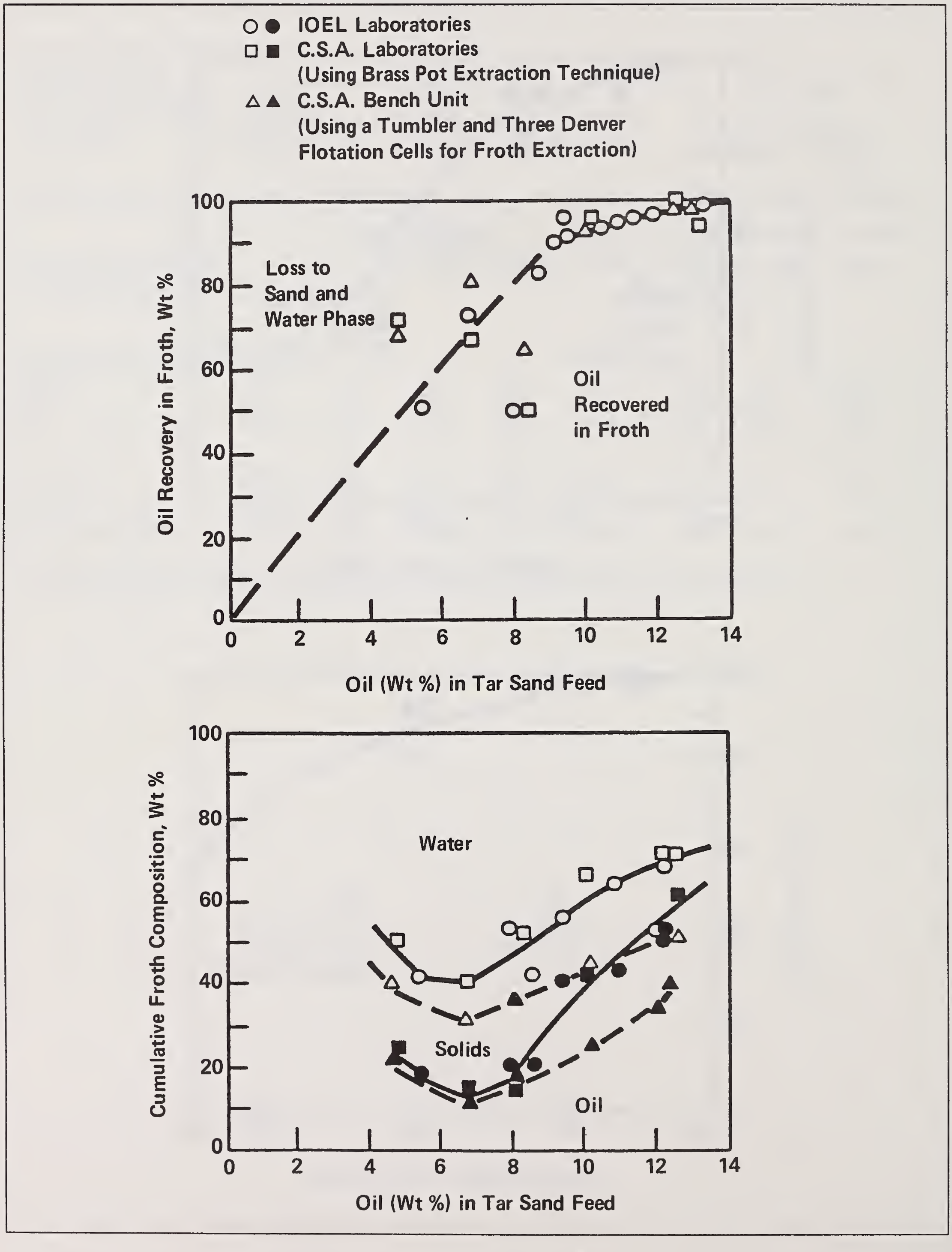


Table 6-35

Summary of Electrical, Chemical and Colloidal Parameters of the Water Phase from Separation of the Athabasca Tar Sands

Tar Sand (Designation)	**Plant Feed**	**Good**	**Inter-mediate**	**Bad**	**Bench No.1**	**--- Unit Feeds - Run No. ---**			
						--- 6 ---		**7**	**9**
						Can #1	**Can #2**		
Water Phase									
Hydroxyl ion: pH_2	8.2	7.9	8.5	5.9	3.7	7.4	7.9	8.3	8.1
Zeta Potential ZP_1	26	35	34	21	19	19	-	23	18
Zeta Potential ZP_2	34	52	59	25	22	20	-	36	26
Conductance, C_1	816	1054	952	782	1224	432	-	517	296
Oven Dried Salt, Wt %									
"Soluble"	0.055	0.056	0.053	0.074	0.105	0.035	-	0.025	0.017
"Precipitate"	0.075	0.333	0.225	0.000	0.000	0.012	-	0.237	0.024
Total (sum)	**0.130**	**0.389**	**0.278**	**0.072**	**0.100**	**0.048**	**-**	**0.262**	**0.041**
Dry Heated Salt, Wt %									
"Soluble"	0.042	0.042	0.040	0.057	0.078	0.026	-	0.020	0.013
"Precipitate"	0.057	0.252	0.168	0.000	0.000	0.009	-	0.182	0.016
Total (sum)	**0.099**	**0.294**	**0.208**	**0.052**	**0.076**	**0.035**	**-**	**0.202**	**0.029**
Sulphate, Wt %	0.020	-	-	-	0.072	0.031	-	0.011	0.009
Calcium, mg/l	5	-	3	-	124	27	16	5	10
Magnesium, mg/l	7	-	2	-	121	30	21	7	11
Total (sum), mg/l	**12**	**-**	**5**	**-**	**245**	**57**	**37**	**12**	**21**
Whole Salt ≡ 12 Washings									
Dry Heated Salt, Wt %									
"Soluble"	0.083	0.060	0.066	0.088	0.102	0.056	-	0.046	0.069
"Precipitated"	0.096	0.389	-	0.154	0.0002	0.152	-	0.306	0.120
Total (sum)	**0.179**	**0.449**	**-**	**0.242**	**0.102**	**0.208**	**-**	**0.352**	**0.189**

Table 6-36

Processability Summary of Beaver River Tar Sands

Tar Sand (Designation)	Plant Feed	Good	Inter-mediate	Bad	Bench No. 1	- - - Unit Feeds - Run No. - - -			
						- - - 6 - - -		7	9
						Can #1	Can #2		
No Aeration Froth									
Solids/Oil Ratio	0.32	0.19	0.35	3.08	0.29	0.24	0.10	0.29	0.19
Water/Oil Ratio	0.89	0.64	0.76	4.44	0.91	0.99	0.81	0.81	0.58
Oil Recovery, Wt %	89.1	75.9	86.8	7.0	33.6	39.0	66.1	88.2	86.5
No + 1st Aeration Froths									
Solids/Oil Ratio	0.38	0.25	0.40	5.41	0.35	0.35	0.29	0.40	0.25
Water/Oil Ratio	1.08	0.70	0.91	9.40	1.08	1.09	1.39	1.07	0.77
Oil Recovery, Wt %	92.5	91.5	93.5	30.6	86.7	89.5	90.3	92.3	90.8
No + 1st + 2nd Aeration Froths									
Solids/Oil Ratio	0.50	0.34	0.47	5.79	0.44	0.41	0.33	0.57	0.34
Water/Oil Ratio	1.51	1.01	1.19	9.95	1.37	1.22	1.80	2.21	0.91
Oil Recovery, Wt %	95.1	93.8	95.8	51.4	93.0	93.5	95.5	93.8	96.5
Oil Loss in Water Phase	3.7	4.8	3.5	26.5	2.2	4.2	2.8	4.3	2.0
Oil Loss in Sand Phase	1.2	1.4	0.7	22.1	4.8	2.3	1.6	1.9	1.5

Table 6-37

Effect of Mixing Speed on Tar Sand Processability (Beaver River Plant Feed : 11% Oil, 4% Water, 16% Clay, 69% Sand)

Mixing Speed, rpm	**120**	**350**	**500**	**600**	**800**	**1000**
Results, Wt %						
No Aeration						
Froth Composition						
Water	39.4	37.3	33.7	44.1	40.2	37.4
Solids	14.4	12.2	8.5	11.2	14.4	7.2
Oil	46.2	50.5	57.9	44.7	45.4	55.4
S/O Ratio	0.31	0.24	0.16	0.25	0.32	0.14
W/O Ratio	0.85	0.74	0.58	0.99	0.89	0.69
Oil Recovery	23.1	60.2	66.9	83.9	89.1	76.3
No and First Aeration						
Froth Composition						
Water	35.1	44.0	42.6	47.6	48.0	39.9
Solids	18.1	15.8	13.7	11.5	14.3	11.7
Oil	46.8	40.2	43.7	40.8	37.7	48.4
S/O Ratio	0.39	0.40	0.32	0.28	0.38	0.25
W/O Ratio	0.75	1.10	0.99	1.17	1.08	0.83
Oil Recovery	82.8	90.7	90.1	91.8	92.5	92.8
No, First and Second Aerations - Total Froth						
Froth Composition						
Water	35.7	46.8	49.3	52.8	55.6	42.5
Solids	19.8	17.3	15.4	13.9	14.8	18.7
Oil	44.5	35.9	35.3	33.3	29.6	38.8
S/O Ratio	0.44	0.48	0.44	0.42	0.50	0.48
W/O Ratio	0.80	1.31	1.40	1.58	1.51	1.10
Oil Recovery	92.3	94.3	94.2	94.1	95.1	95.4
Oil Loss to:						
Water Phase	6.5	4.4	4.5	4.3	3.7	3.8
Sand Phase	1.2	1.3	1.3	1.6	1.2	0.8
pH of First Water Phase	8.2					

The most important result was that 89% oil recovery was achieved with Beaver River plant feed in a primary separating stage with no air addition other than perhaps that entrained in mixing in the laboratory technique. The agitation energy in terms of mixer speed adopted in the modified Brass Pot procedure was therefore the optimum 800 rpm.

Froth quality from this separation is plotted in Figure 6-30, and it can be seen that both the water and solids increase with aeration. Water to oil ratio also increased with mixing speed up to 400 rpm. The results of 0.79 water to oil and 0.24 solids to oil ratios with no air addition in primary separation was also typical of other Beaver River Tar Sands reveals at the same oil recovery level.

Table 6-38

Three Stage Separation of Tar Sands

Separation Stage	Air (cu ft/lb) Tar Sand	Oil Recovery In Froth, Wt%	--------- Froth ---------	
			W/O	S/O
Primary	None	89	0.8	0.25
Secondary	0.38	92	1.0	0.35
Tertiary	0.38	95	1.5	0.46

In the modified Pot separation at optimum mixing of 800 rpm, oil recovery in secondary and tertiary separations with air addition resulted in significant deterioration in froth quality for only small oil recovery gains, as illustrated in Table 6-38.

An economic limiting separation is therefore indicated, that is dependent on the ability of froth processing to eliminate water and solid contaminants, as well as equipment for incremental oil recovery.

6-23 Selective Mining

Dr. Karl Clark's original process development in primary hot water flotation was shown to be sensitive to the amount of fines in the system. This was discussed before, in Figure 6-1.

As a verification of this effect, various amounts of a Beaver River clay lens were added with plant feed tar sands in the laboratory separations, in the modified Pot Procedure,. The results of one example is shown in Table 6-39, and is plotted in Figure 6-31.

The oil recovery in primary froth declined with increasing amounts of fines in the system. Extrapolation of data to low fines content (~5%) in the feed indicates that incrementally higher oil recoveries in the order of perhaps 5% may be achieved if clay could be reduced by selective mining. Strip mining with scrapers, that has been proposed by Syncrude, lends itself more to selective mining for eliminating as much of the clay strata as possible, than Bucket wheel mining.

The convergence of the oil recovery data in Figure 6-31 for primary and primary + secondary separations indicates that equivalent oil recoveries may be obtained in just primary separation with selective mining reducing the amount of clay in the feed, thus making the secondary

Figure 6-29

Increasing Mixing Speed and Aeration Increases Oil Recovery

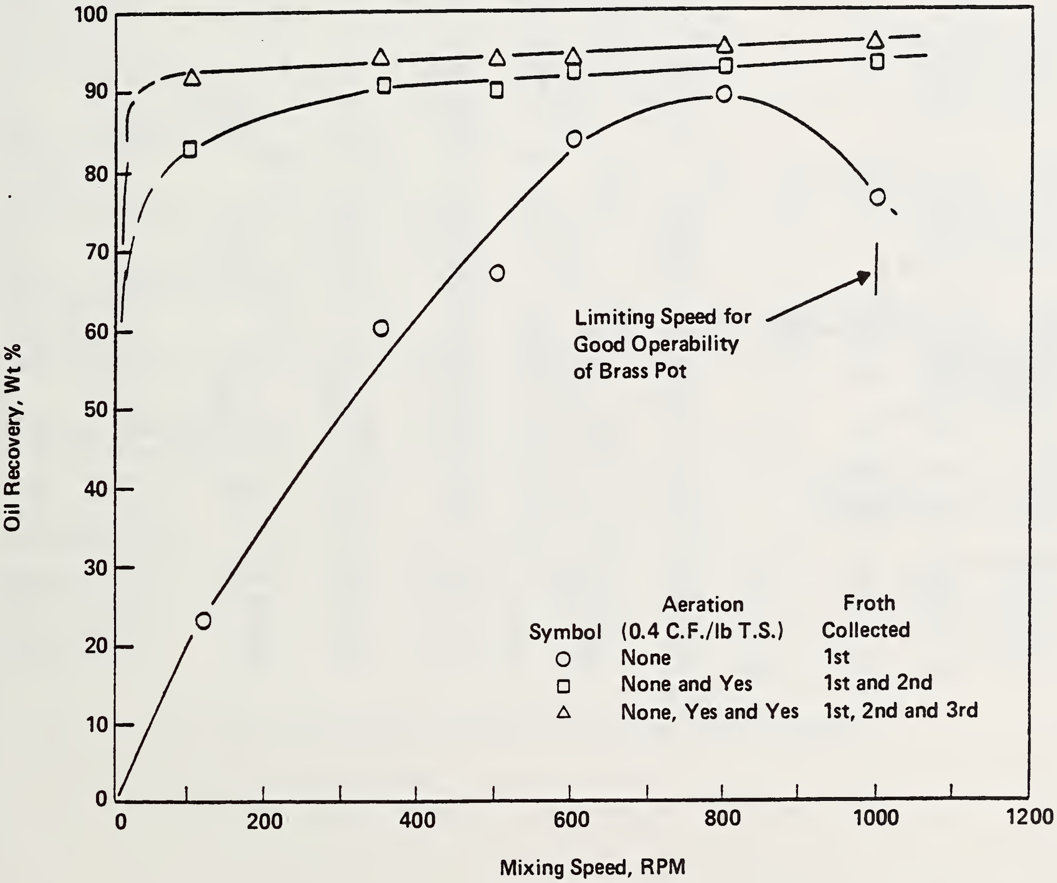


Table 6-39

Effect of Clay on Processability of Beaver River Tar Sands (Plus 0.12 Wt % on Tar Sand Sodium Hydroxide Addition for pH Control)

Feed Blend, Wt %							
Plant Feed Tar Sand (Fresh)	100	95	90	85	80	75	70
Clay Lens (Water-Wet)	0	5	10	15	20	25	30
Components in Blend							
Oil	11.0	10.5	9.9	9.4	8.8	8.3	7.7
325 - Solids	16.3	19.8	23.3	26.7	30.2	33.7	37.2
No Aeration Froth							
Solids/Oil Ratio	0.16	0.18	0.16	0.13	0.14	0.62	1.65
Water/Oil Ratio	0.44	0.39	0.39	0.54	0.56	1.76	3.38
Oil Recovery, Wt %	87.9	84.6	83.1	71.6	62.9	31.2	10.9
No + 1st Aeration Froth							
Solids/Oil Ratio	0.19	0.22	0.19	0.23	0.28	0.71	1.45
Water/Oil Ratio	0.46	0.47	0.46	0.70	0.83	1.65	2.88
Oil Recovery, Wt %	90.7	90.1	89.6	89.2	89.4	86.0	50.0
No + 1st + 2nd Aeration Froth							
Solids/Oil Ratio	0.27	0.25	0.24	0.32	0.34	1.21	2.25
Water/Oil Ratio	0.50	0.53	0.53	0.93	1.06	2.32	3.75
Oil Recovery, Wt %	95.2	90.5	89.9	89.4	90.2	86.1	62.6
Oil Loss in Water Phase	4.6	7.8	7.6	8.7	8.0	11.8	25.6
Oil Loss in Sand Phase	0.2	1.7	2.5	1.9	1.8	2.1	10.9
Water Phase: pH	9.9	10.3	10.0	10.3	9.7	9.6	9.5
Calcium, mg/l	5	11	21	20	23	12	9
Magnesium, mg/l	8	17	22	28	28	9	8
Total, mg/l	13	28	43	48	51	21	17

Table 6-40

Extreme pH effects on Processability of Tar Sands

Tar Sand (Designation)	Plant Feed		Bench No. 1		Unit Feeds - Run No.					
					6		7		9	
Additive	HCl	NaOH	NaOH	NaOH	HCl	NaOH	HCl	NaOH	HCl	NaOH
Amount, Wt % on Tar Sand	0.11	1.20	0.04	1.20	0.11	1.20	0.11	1.20	0.11	1.20
No Aeration Froth										
Solids/Oil Ratio	6.44	0.14	0.22	0.40	0.55	5.25	-	0.46	2.12	0.14
Water/Oil Ratio	25.56	0.75	1.76	1.33	5.00	15.00	-	1.67	9.40	0.71
Oil Recovery, Wt %	1.0	51.0	38.2	6.8	0.4	0.8	0	5.5	1.9	51.3
No + 1st Aeration Froths										
Solids/Oil Ratio	4.50	0.32	0.78	0.53	0.52	0.18	3.92	0.43	2.51	0.22
Water/Oil Ratio	6.24	1.37	2.10	0.93	2.28	0.93	10.32	1.49	7.60	0.91
Oil Recovery, Wt %	27.6	98.2	93.0	61.4	50.2	90.1	9.9	83.2	16.4	92.7
No + 1st + 2nd Aeration Froths										
Solids/Oil Ratio	4.58	0.40	0.79	0.40	0.82	0.31	5.45	0.45	3.43	0.25
Water/Oil Ratio	6.19	1.49	2.24	0.83	2.56	1.06	10.72	1.52	7.00	0.99
Oil Recovery, Wt %	38.0	98.2	95.1	96.4	71.2	92.7	20.5	90.0	36.1	92.7
Oil Loss in Water Phase	57.1	1.5	3.2	3.4	24.0	7.2	68.1	5.2	54.4	3.3
Oil Loss in Sand Phase	4.9	0.3	1.7	0.2	4.8	0.1	11.4	4.8	9.5	4.0
Water Phase: pH[2]	4.9	(12.8)	5.3	(12.9)	5.0	(12.8)	4.8	(12.8)	5.7	(12.8)
Zeta Potential, ZP[1]	15	(1)	23	(1)	10	(1)	16	(1)	18	(1)
Conductance, C[1]	2584	(1)	1972	(1)	3128	(1)	3196	(1)	2992	(1)
Calcium, mg/l	97	11	76	16	184	11	108	11	135	11
Magnesium, mg/l	152	23	66	13	135	11	155	15	164	13
Total, mg/l	**249**	**34**	**142**	**29**	**319**	**22**	**263**	**26**	**299**	**24**

(1) Specific Conductance is very high; water phases black and thermal overturn make zeta potential measurements impossible.

NOTE: Values in parenthesis are maxima readings on instrument.

separation stage a minor clean up. This proposed technique is essentially a means of increasing the grade of mined oil sands, Figure 6-32.

Froth quality also shows lower contamination with greater than ~9 grades and less than about 25% fines, however, grades and higher fines will results in dramatic deterioration of performance in terms of both oil recover and froth quality.

6-24 pH Control

The effect of pH on "primary" (no aeration) separation of Beaver River tar sands is shown in Figure 6-33. Data on no additives is summarized in Table 6-36, and at extreme pH's in Table 6-40, with sodium hydroxide and hydrochloric acid addition . The plot shows that good oil recovery in primary froth can be obtained at pH's from 8-12. Outside this region good processability is lost very rapidly. This ws attributed to the deleterious effect of polyvalent ions, e.g. Table 6-41.

Table 6-41

Acid Separations gave High Ca + Mg Contents in the Separation Water Phaseand Poor Processability

Tar Sand Designation	Separation, pH	Calcium + Magnesium mg/l	Oil Recovery Primary	Primary + Secondary
Plant Feed	4.9	249	1	28
Unit Feed - Run No. 6	5.0	319	0.5	50
Unit Feed - Run No. 7	4.8	263	0	10
Unit Feed - Run No. 9	5.7	299	2	16

The effect of pH on combined primary (no aeration) and secondary (aeration) separations is shown in Figure 6-34. The workable pH region is now extended slightly 7.5-12.5. However, a maximum in oil recovery is indicated at about 9. ± 1 pH, which was not evident in Figure 6-33 for primary separation. The shape of the pH curves versus oil recovery are similar to other data obtained previously.

Solids and water to oil ratios are plotted as a function of pH in Figure 6-35 for primary separations. Solid/oil ratios show a low flat minimum over a wide range of pH, i.e. 6.5-12.5. However, a minimum pH was found for water to oil ratios at about 9.5 ± 1, which also appeared to be the optimum pH range for good processability.

The same general relationships are found for froth qualities as a function of pH for primary plus secondary separations, Figure 6-36. The solids to oil ratio, however, did show a slight but significant decrease with increasing pH from 7 to 13. In general average values were slightly higher, compare Figures 6-35 and 3-36.

Operations at a constant pH of 9.9 again showed consistent froth qualities of tar sands with >9% oil and <30% fines contents, Figure 6-37.

Two of the eight tar sands, i.e. "Bad" and "Bench No. 1" tar sands, were acid. Two samples of Unit Feed - Run No. 6 were received and these were slightly different in pH and behaviour."Bad" tar sands (~6% oil) was not completely regenerable with alkaline additives, i.e. 84% oil recovery in a two-stage process. "Bench No. 1" (~11% oil) was readily regenerable with alkaline additives in spite of an even lower initial pH of 3.7. and high soluble Ca and Mg content. Processability data for this tar sand alone, Figure 6-38, showed that it was somewhat unusual in that it separated moderately well under acid conditions.

Table 6-42

Effect of Calcium and Magnesium Addition on Processability of Beaver River Plant Feed Tar Sands (0.08 Wt % on Tar Sand of Sodium Hydroxide was added in Mixing for pH Control)

Polyvalent Ion Solution:		----- $CaSO_4$ -----				---- $CaSO_4$ ----				--- $MgSO_4$ ---		
In Mixing (mg/l)	-	100	200	300	400	------ 400 ------				300	300	300
In Flooding (mg/l)	-	100	200	300	400	------ 400 ------				300	300	300
Corrective Additive: Sodium												
	-	-	-	-	-	--- EDTA ---		--- $P_2O_{10}^{5-}$ ---		-	--- $P_2O_{10}^{5-}$---	
In Mixing (Wt % on Tar Sand)	(1)	-	-	-	-	-	0.5	-	0.5	-	-	0.8
In Flooding (Wt % on Tar Sand)	-	-	-	-	-	0.5	-	0.4	-	-	0.5	-
Aeration Froth												
Solids/Oil Ratio	0.16	0.14	0.16	0.24	2.01	0.40	0.31	0.09	0.14	1.69	0.10	0.06
Water/Oil Ratio	0.44	0.45	0.82	1.08	4.61	1.68	1.56	0.47	0.54	4.66	0.52	0.51
Oil Recovery, Wt %	87.9	83.1	72.0	51.4	6.9	30.9	33.1	69.3	83.9	5.3	47.0	86.9
No + 1st Aeration Froth												
Solids/Oil Ratio	0.19	0.21	0.31	0.80	1.89	0.98	0.78	0.14	0.19	1.38	0.20	0.09
Water/Oil Ratio	0.46	0.66	1.25	2.38	3.99	2.64	2.53	0.59	0.58	2.85	0.90	0.58
Oil Recovery, Wt %	90.7	90.3	82.9	65.8	39.2	64.9	84.7	89.1	87.7	39.8	88.3	90.2
No + 1st + 2nd Aeration Froths												
Solids/Oil Ratio	0.27	0.26	0.43	1.13	2.50	1.65	1.18	0.18	0.22	2.30	0.23	0.11
Water/Oil Ratio	0.50	0.83	1.70	3.39	4.93	3.53	3.29	0.66	0.66	3.80	0.95	0.64
Oil Recovery, Wt %	95.2	90.9	83.2	72.2	50.9	84.2	88.5	90.2	88.0	47.8	90.1	90.7
Oil Loss in Water Phase	4.6	8.5	13.3	19.1	41.0	9.1	7.2	8.3	10.5	33.8	9.2	7.9
Oil Loss in Sand Phase	0.2	0.6	3.5	8.7	8.1	6.7	4.3	1.5	1.5	18.4	0.7	1.4
Water Phase: pH	9.9	9.5	9.4	9.2	9.4	8.1	8.1	9.5	9.6	8.4	9.5	9.6
Calcium, mg/l[2]	5	5	11	24	54	-	-	-	-	(0)	-	-
Magnesium, mg/l[2]	8	6	6	5	5	-	-	-	-	(128)	-	-
Total, mg/l[2]	13	11	17	29	59	-	-	-	-	(128)	-	-

(1) 0.12 Wt % sodium hydroxide was added in this experiment.

(2) Determinations are questionable in the presence of high concentrations of sequestering agents added, and with magnesium salt addition.

Unit Feed- Run No. 6 was a blend of two separately mined tar sands, see Table 6-34. One component had been stock piled (open to the atmosphere), before blending. Further, the blend had been stored in a root cellar in the Mildred Lake escarpment. The pH of the two samples received was slightly alkaline, but variable: 7-8. It did not process too well in primary (no aeration), which was attributed to higher than normal content of soluble calcium and magnesium, Table 6-35. However, in a two stage process, or with adjustment to slightly more alkaline conditions in primary separation, good processability was achieved.

6-25 Divalent Metal Ions

(a) Naturally Occurring

EDTA titrations were used for the determination of soluble calcium and magnesium ions in the separation water phase. From these data, it was observed that primary processability declined with increasing amounts of soluble calcium and magnesium ions in the separated water phase. Some results, to illustrate this point, are plotted in the upper graphs of Figure 6-39. In the lower plots, combined primary and secondary separations are shown to be far less sensitive to the presence of these deleterious ions .

The overall relationship of the soluble calcium and magnesium contents to pH found is similar to the effect of fines on processability, Figure 6-1. This comparison shows that a relationship between the amount of water soluble divalent metal ions in the system and processability may exist.

(b) Acid Separations

Acid (sulphuric) conditions generated in tar sands through oxidation of sulphides will result in higher amounts of soluble divalent metal ions. The same effect is observed with acid separations utilizing hydrogen chloride (rather than sulphuric), as was shown in the Table 6-41.

Generally, poorer oil recoveries are achieved even with secondary separation involving aeration, Figure 6-34.

(c) Addition in Separation

In order to assess the effect of these divalent metal ions, various calcium and Ca and Mg concentrations in the water used in separation were employed. The results are tabulated in Table 6-42 and plotted in Figure 6-40. These experiments were carried out at approximately a constant pH of 9.5 by sodium hydroxide addition.

The results of our studies show that calcium and magnesium ions are involved in deteriorating processability even in alkaline media and that poorer processability is related to larger amounts of these soluble ions in the separation water phase. The large decreases in ion concentration that occurred in these separations indicate reaction of these ions with other species in the system. Contaminants in the froth are also observed to increase with increasing amounts of these deleterious divalent metal ions in the system, Figure 6-41.

The effect of different magnesium salts/caustic additions were also evaluated to complete the findings, Figure 6-42. As expected the effects are similar to those for Ca salts.

6-26 Correcting Processability

The problem of improving processability by chemical addition may appear complex, but is in fact simplified by regular occurrence of only certain types of deleterious ions in the tar sands. The general solution to the problem is to strike a balance between pH, Na/polyvalent cation ratio, anion types and concentrations to efficiently complex deleterious cations and overcome oil-solid, attachment, at low ionic strengths, while maximizing charge and hydration of surfaces, i.e. dispersion.

This, however, requires correlated data not presently available or in the literature that will result in an integrated relationship of these operative factors with processability, that must hold for all practical cases. Such a relationship should provide a basis for correlations of tar sand processability with monitored process measurements for control of a continuous operation.

Poor processability can therefore result even under optimum pH conditions, if appreciable amounts of divalent ions are present in the system. The best method of correcting for this type of poor processability, is to add complexing agents either in place of or together with caustic to adjust the pH to ~9. Process economics will determine the selection.

Figure 6-30

Increasing Mixing Speed Increases Water in Froth , and Increasing Aeration Increases both Water and Solids

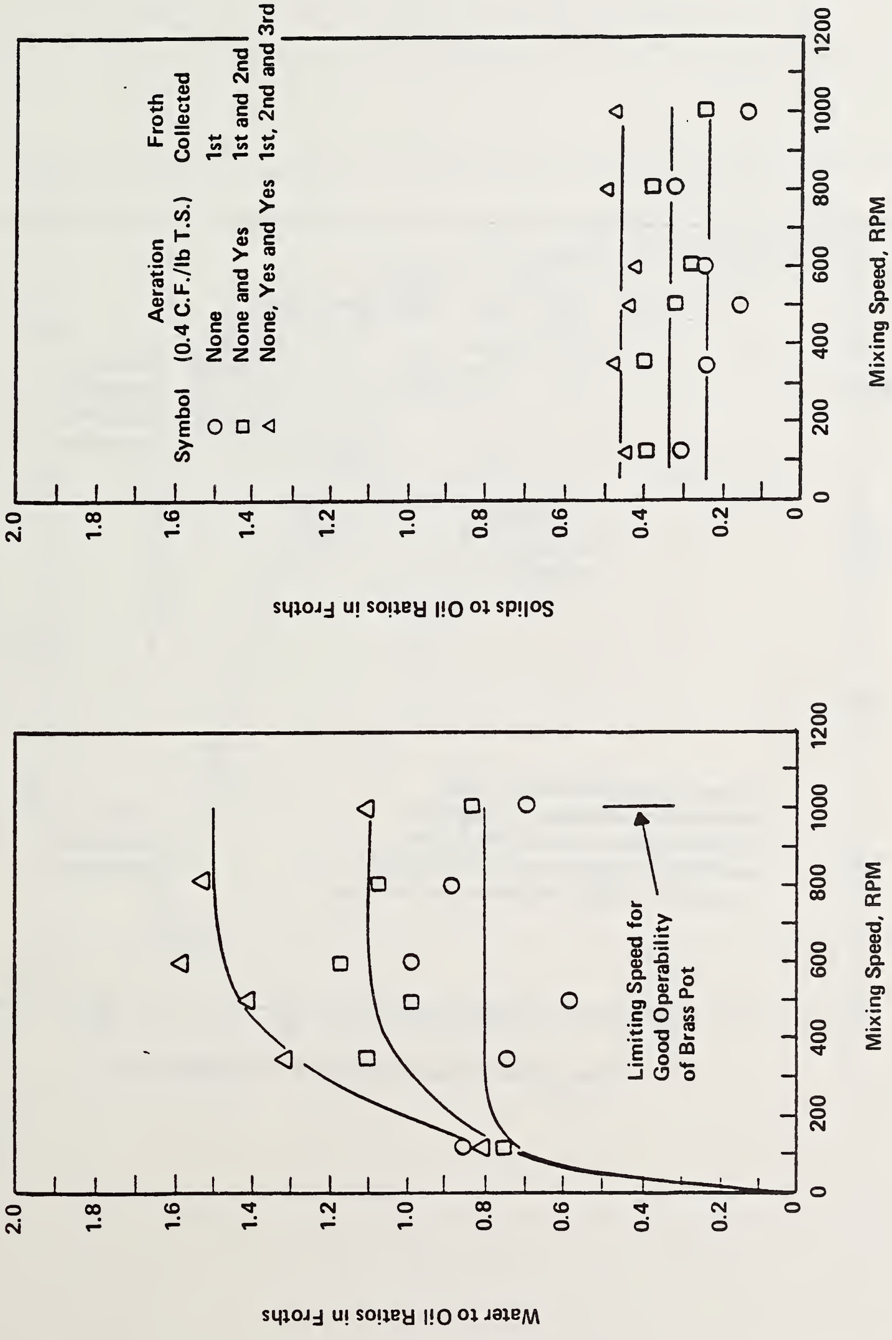


Figure 6-31

Relationship of Processability with Fines Content at a Constant pH of 9.9

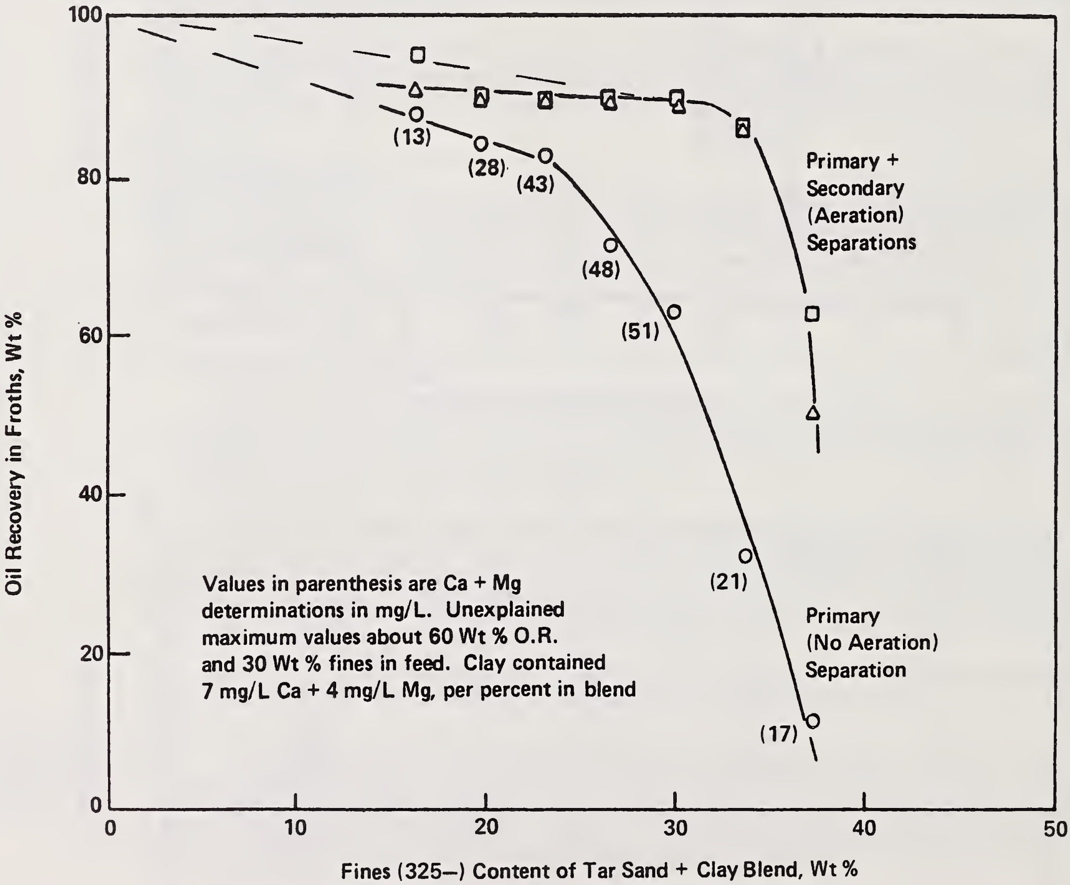


Figure 6-32

Relationship of Processability with Oil Content at a Constant pH of 9.9

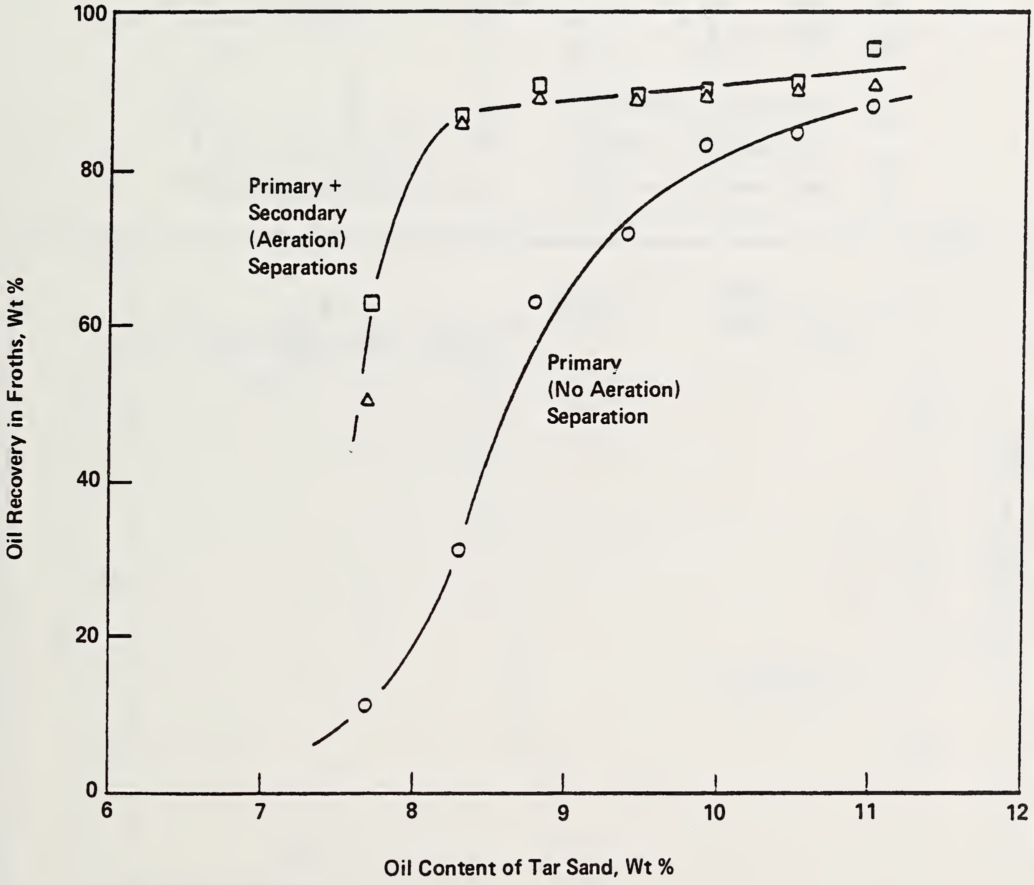


Figure 6-33

pH Effect on Processability of Beaver River Tar Sands (Primary Separation)

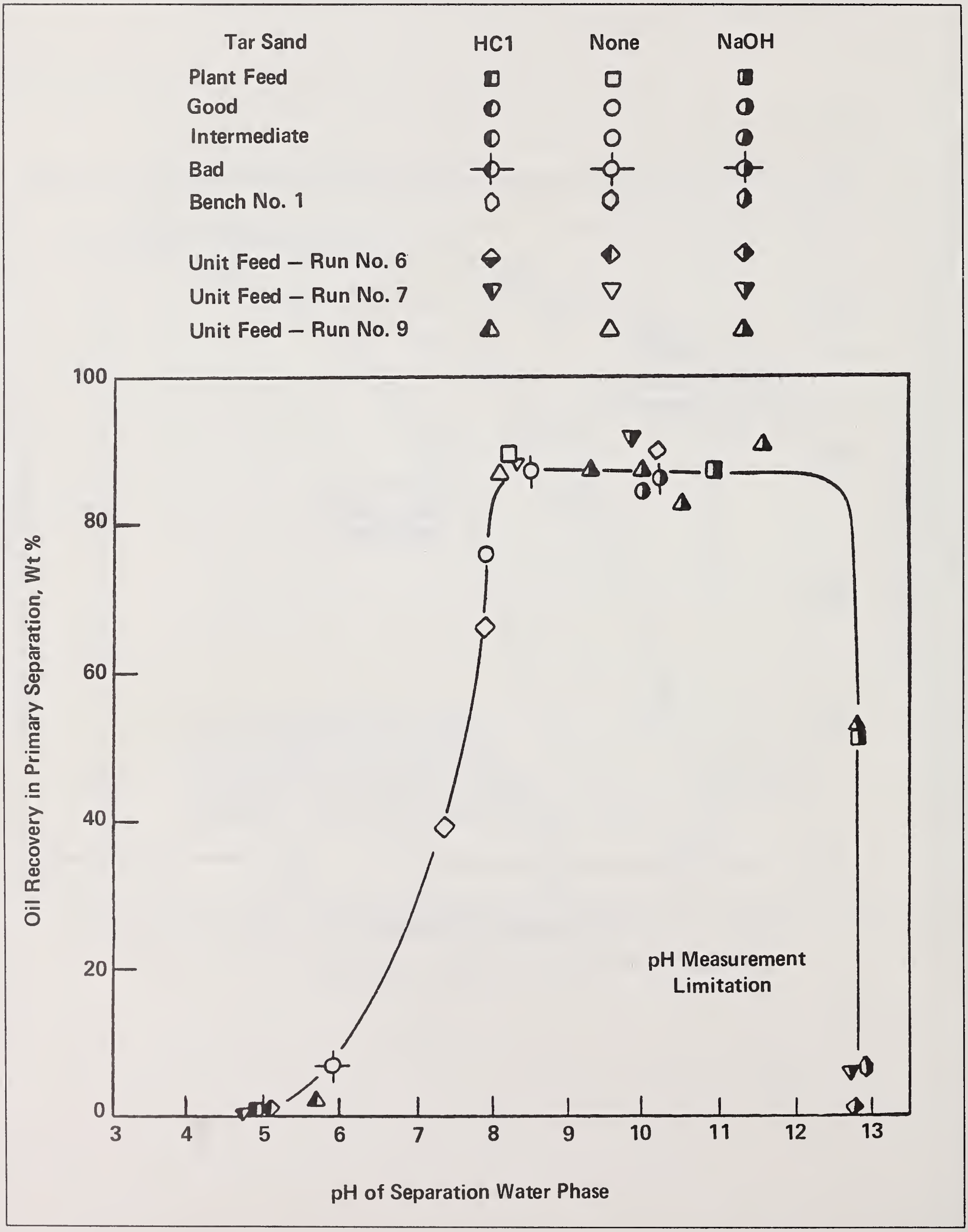


Figure 6-34

pH Effect on Processability of Beaver River Tar Sands (Primary+ Secondary Separation)

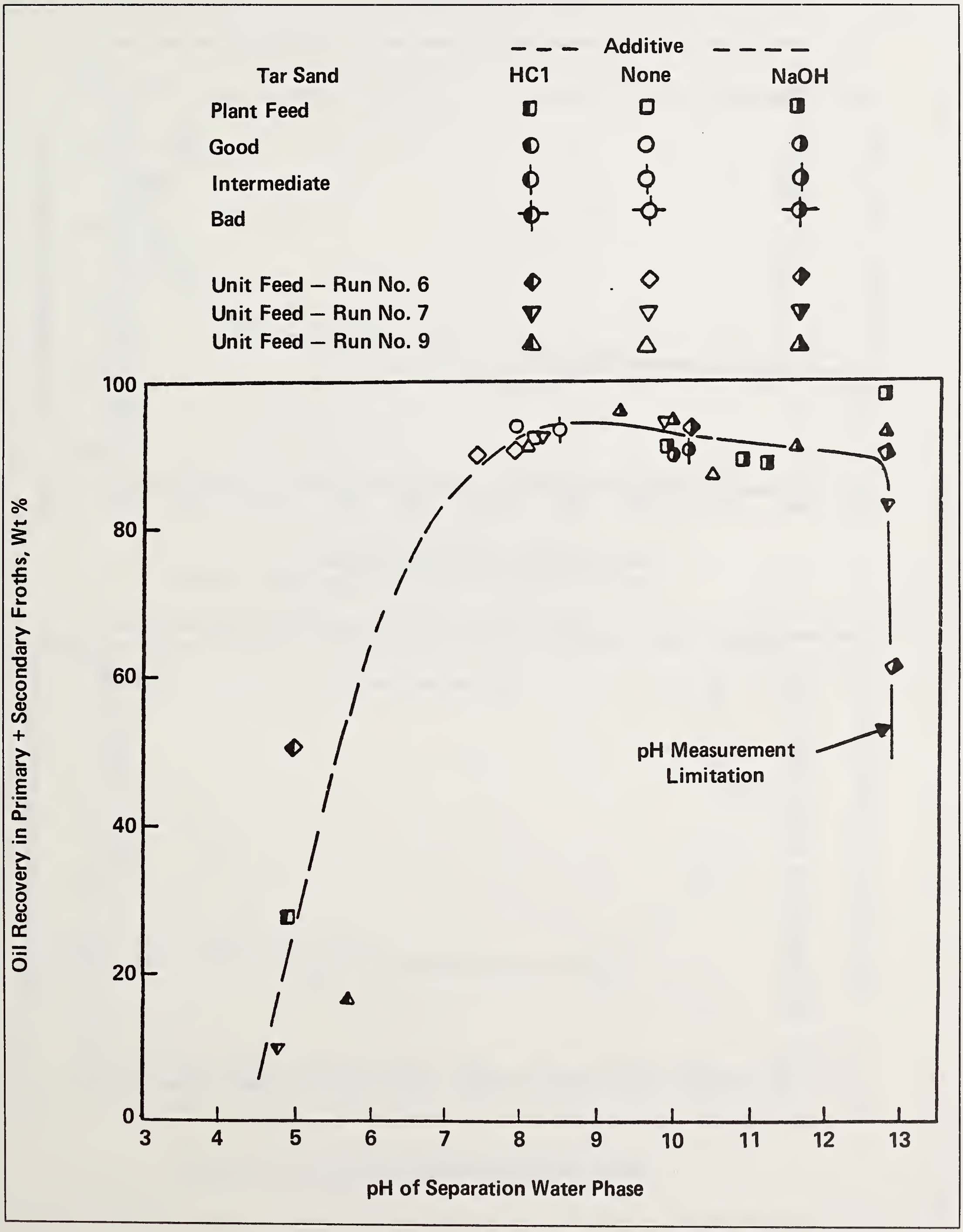


Figure 6-35

Relationship of Froth Contaminants to pH for Beaver River Tar Sands
(Primary Separation)

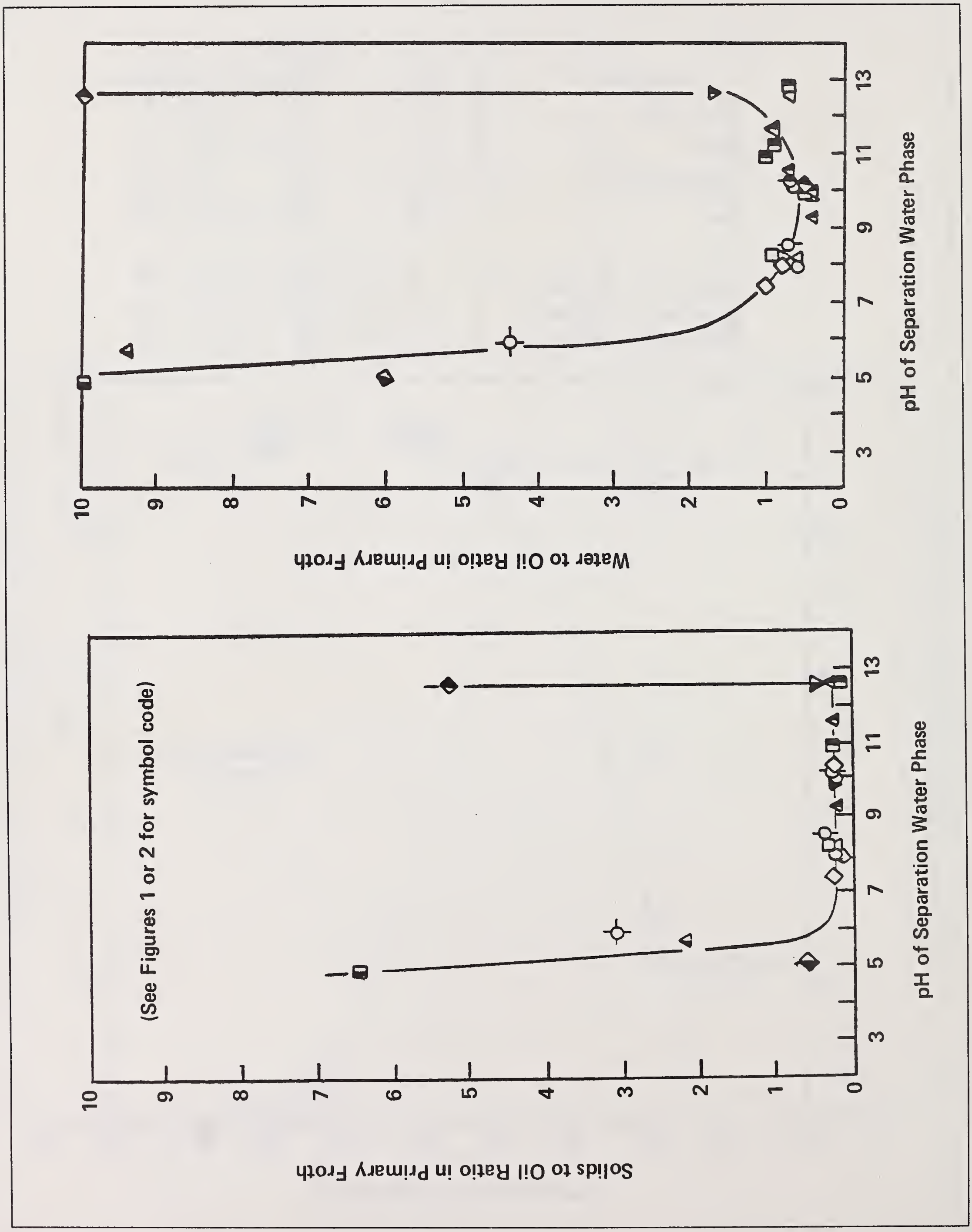


Figure 6-36

Relationship of Froth Contaminants to pH for Beaver River Tar Sands (Primary + Secondary Separation)

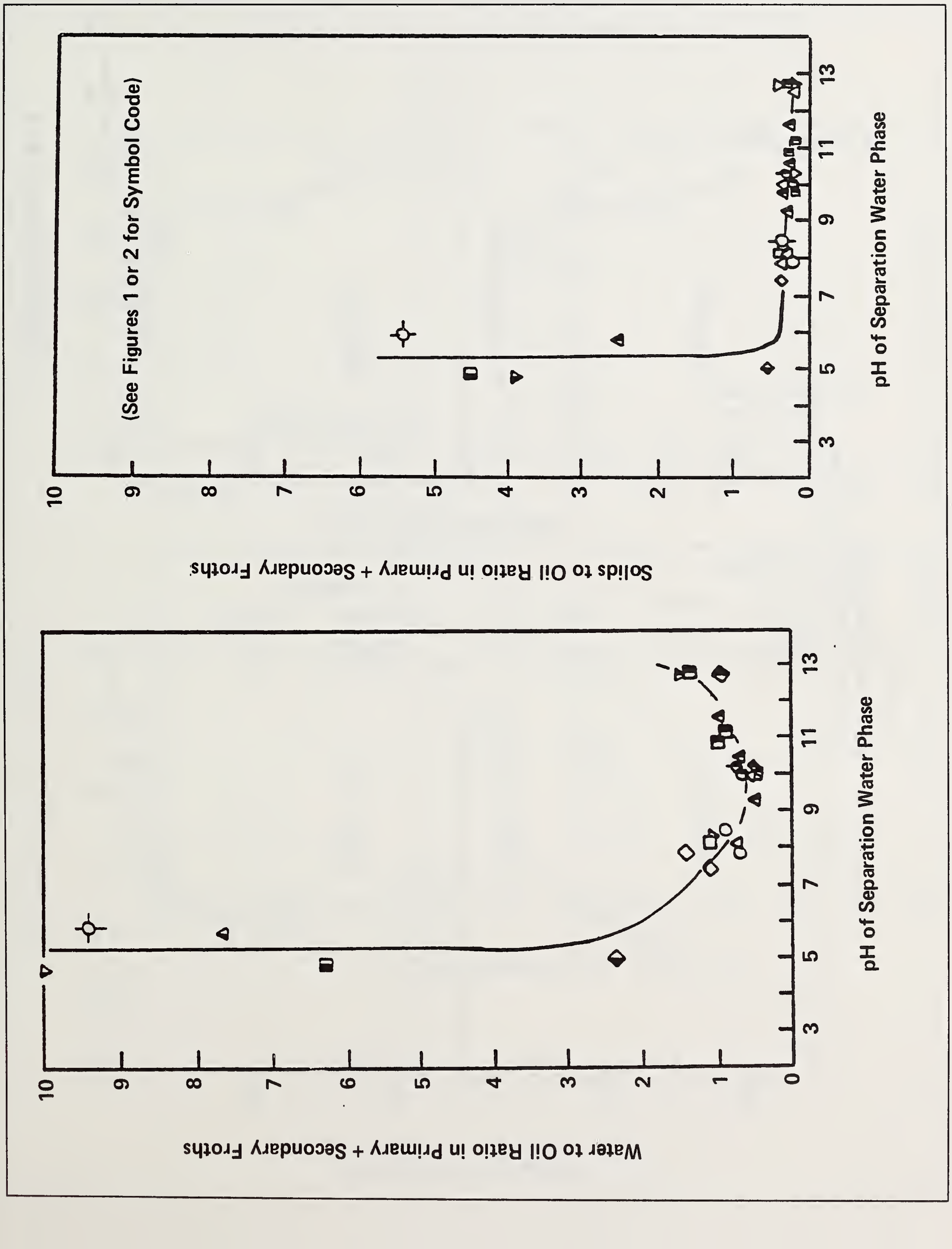


Figure 6-37

Relationship of Froth Quality to Oil and Fines Contents of Feed at a Constant pH of 9.9

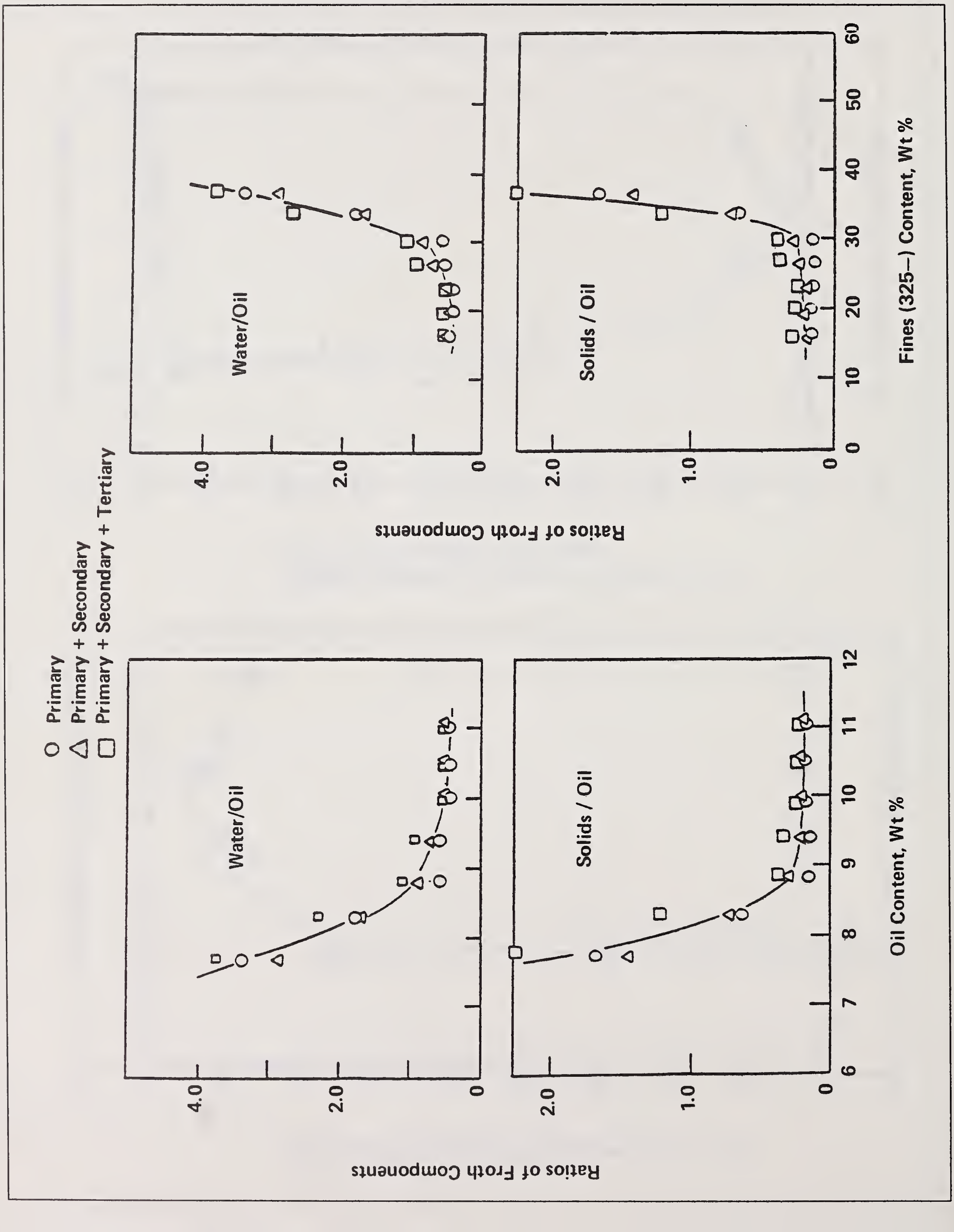


Figure 6-38

Processability of Bench No.1 Tar Sands Is Better in Acid Media Than Other Beaver River Tar Sands but Still Best at pH's 8-11

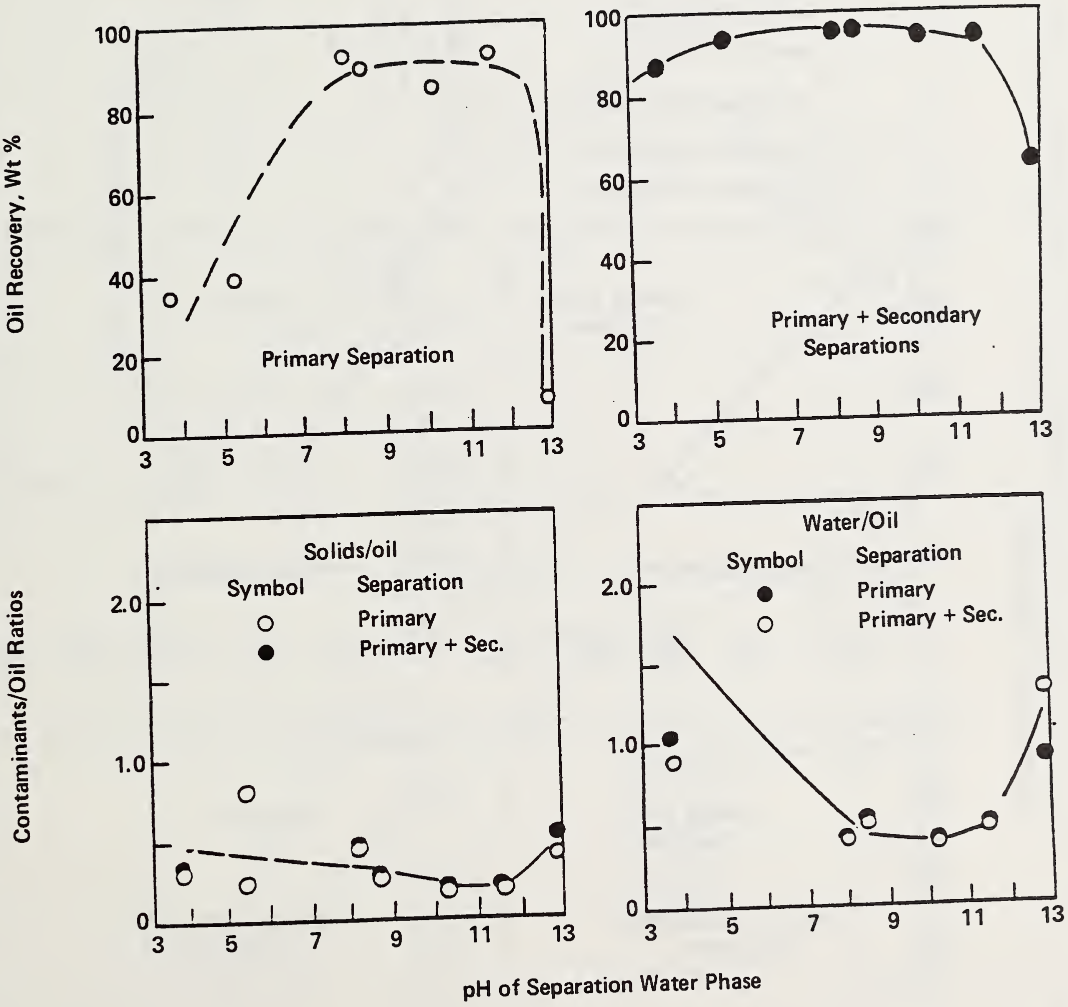


Figure 6-39

Inter-Relationship of Naturally Occurring Soluble Calcium and Magnesium in the Water Phase and Processability (variable pH)

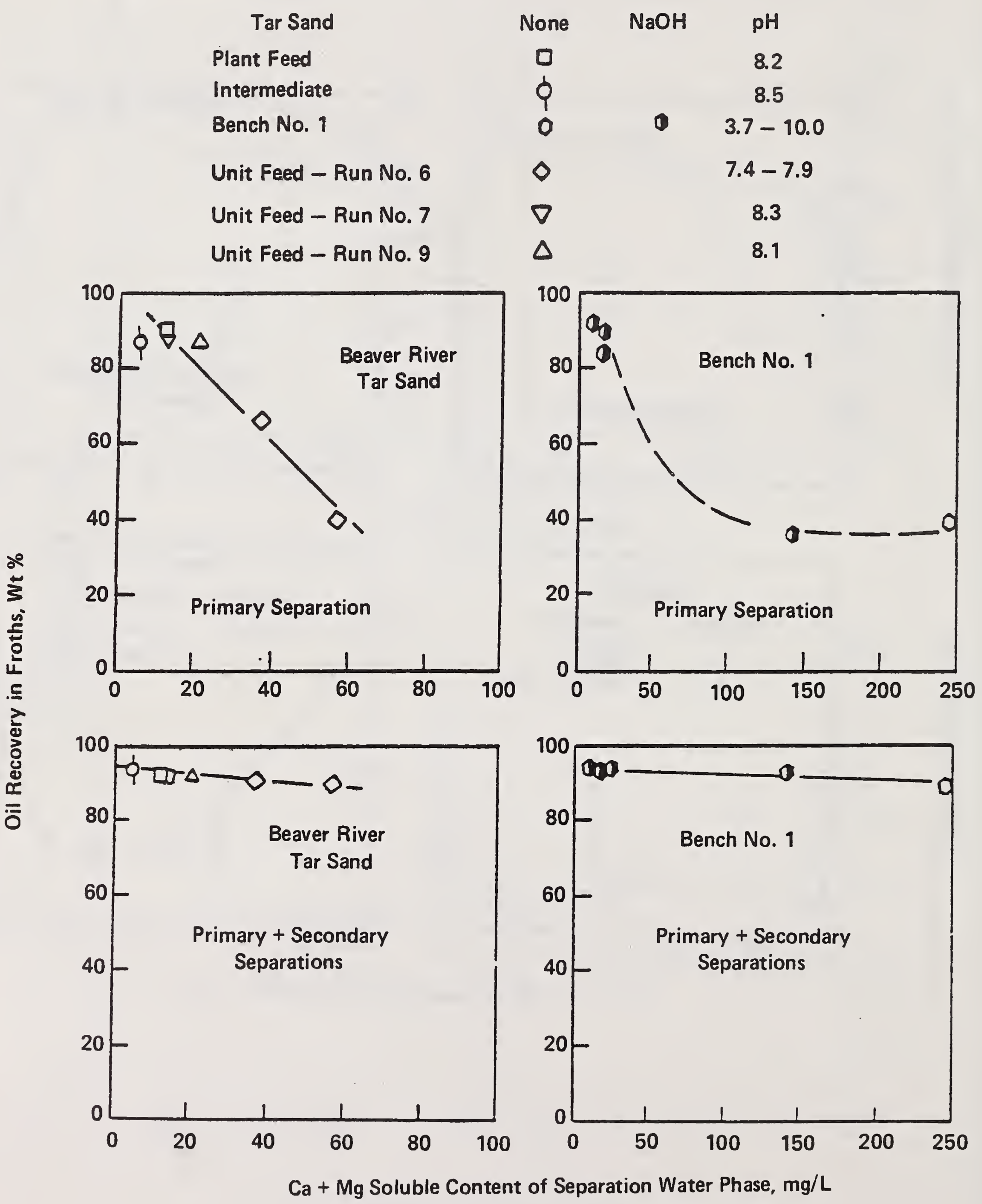


Figure 6-40

Effect of Calcium Addition on Froth Quality of Beaver River Plant Feed Tar Sands at a Constant pH of 9.9

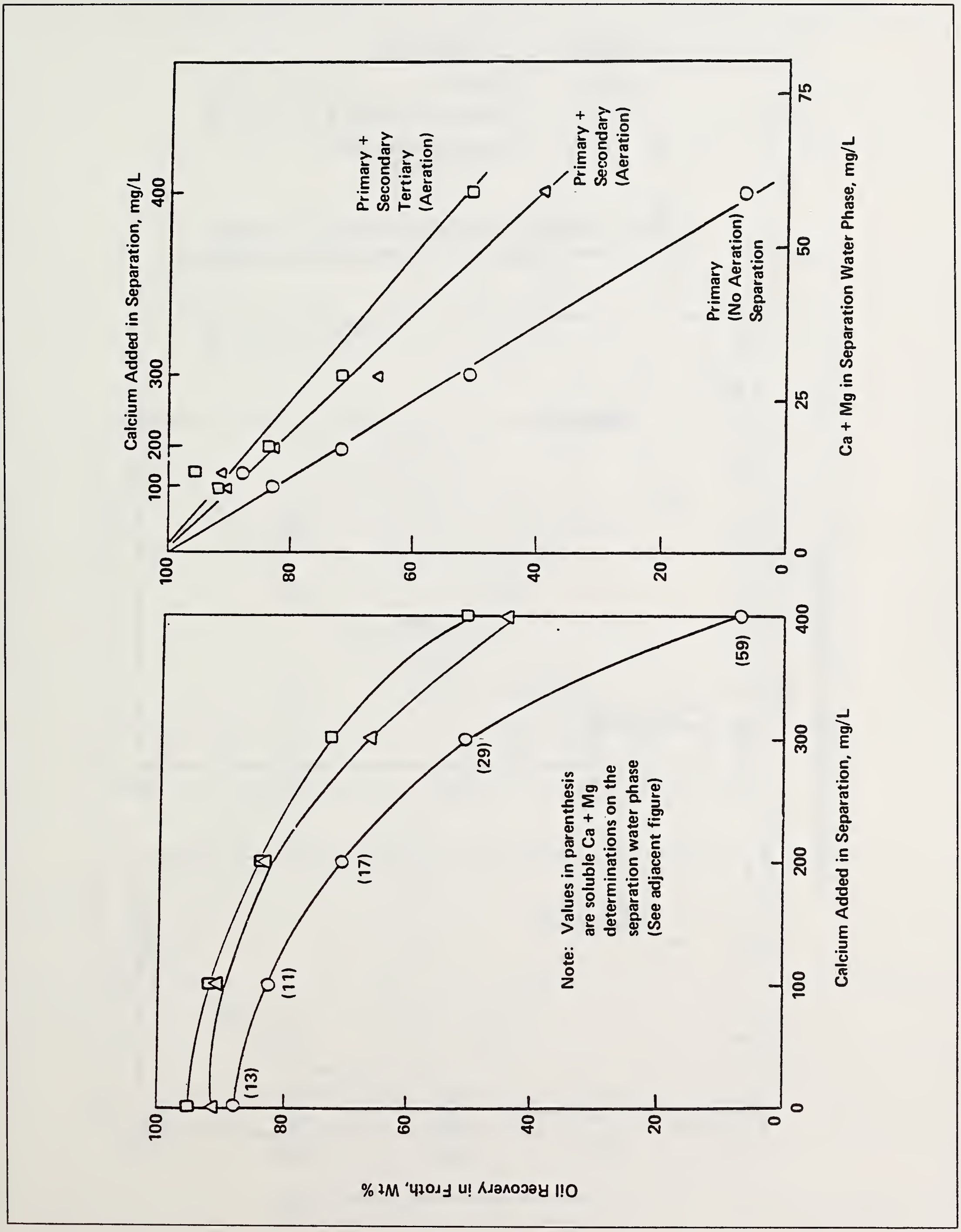


Figure 6-41

Effect of Calcium Addition and Relationship of Soluble Ions to Processability of Beaver River Plant Feed Tar Sand at a Constant pH 9.9

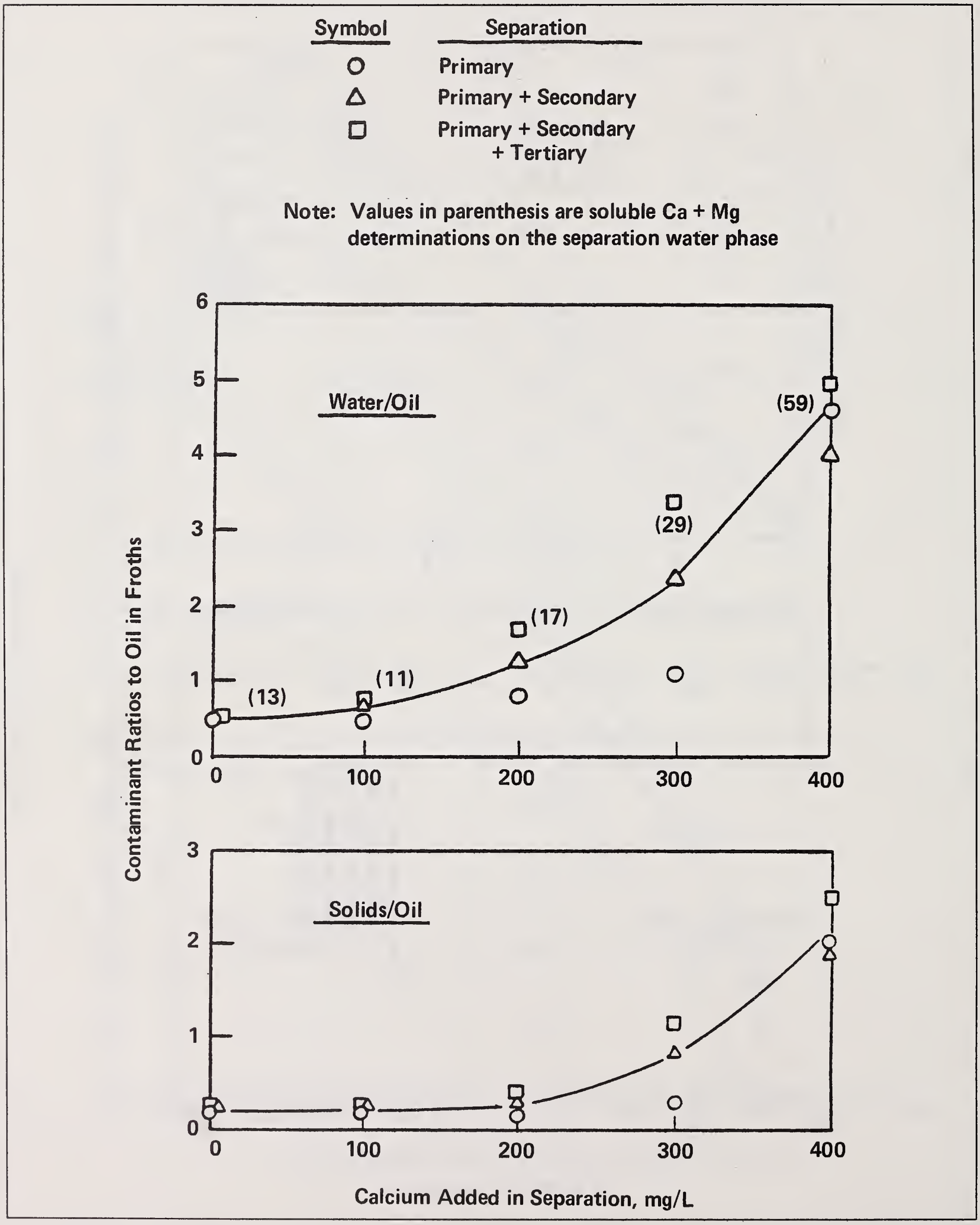


Figure 6-42

Oil Recovery in Hot Water Flotation of Different Oil Sands with the Addition of Magnesium Salts and Sodium Hydroxide

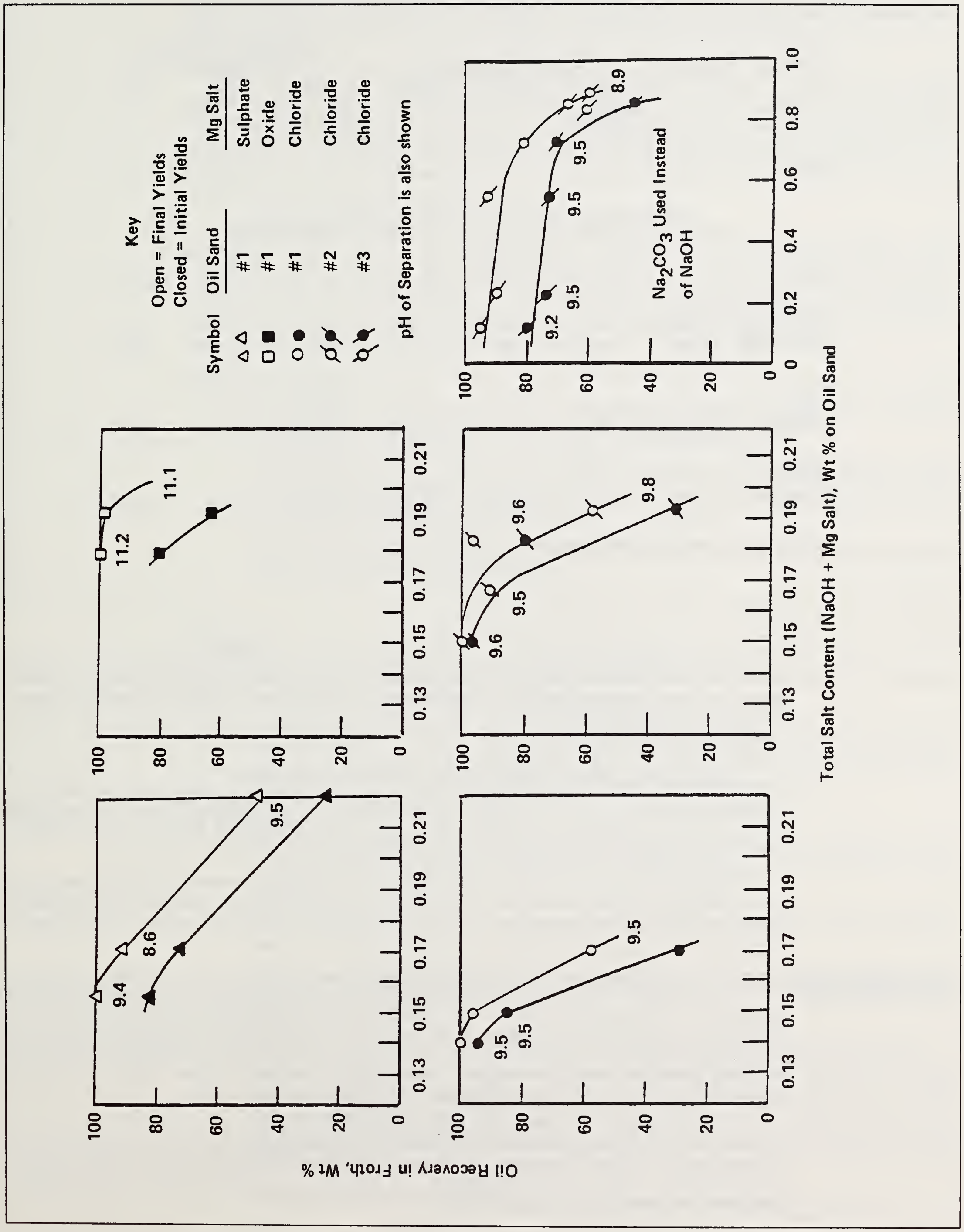


Table 6-43

Complexing Agents Restores Processability in Optimum Alkaline Conditions of 9.5 pH

Additive(1)	Only In	Primary Separation			Primary + Secondary ------- Separation -------		
		Oil Recovery	S/O	W/O	Oil Recovery	S/O	W/O
None	-	88	0.16	0.44	91	0.19	0.46
(With 400 mg/l of Calcium or 300 mg/l of Magnesium)							
None	-	6	1.85	4.64	40	1.64	3.42
EDTA (Na_2)	Flooding	30	0.40	1.68	65	0.98	2.64
EDTA (Na_2)	Mixing	53	0.31	1.56	85	0.78	2.53
Tripoly-phosphate	Flooding	58	0.10	0.50	88.5	0.17	0.75
Tripoly-phosphate	Mixing	85.5	0.10	0.52	89	0.14	0.58

(1) Amounts added were 0.4 - 0.8 Wt % on tar sand.

Some experiments were therefore carried out to verify the benefits of these types of additives, such as disodium ethylenediaminetetraacetate and sodium tripolyphosphate, and under more optimum alkaline conditions. The additions of these "processability correcting agents" were made either in mixing but not in flooding, or in flooding but not in mixing. The average results are summarized in Table 6-43.

It can be seen that either calcium or magnesium cause extensive loss in oil recovery and froth quality in both primary (no aeration) and secondary (aeration) separations at optimum pH conditions of ~9.5. Addition in flooding only of relatively large quantities of complexing agents resulted in improvements, but original processability was not regained. Sodium tripolyphosphate was a better additive than disodium ethylenediaminetetraacetate in these experiments.

Addition in mixing only of complexing agents resulted in substantial improvements in processability. Sodium tripolyphosphate effectively regained the lost processability from addition of calcium or magnesium at a constant pH of ~9.5 maintained by sodium hydroxide addition.

6-27 Summary

A two-stage flotation process involving primary (no aeration) and secondary (aeration) separations is indicated by these studies to be the process approach to the separation of the Athabasca tar sands. The relationship of pH and processability of Beaver River tar sands, in this two-stage process has been defined over a wide range. In practice pH's in the range of 8-12 can be used to achieve good processability with sodium hydroxide addition. Within this flexible region, best performance has been found to occur in the range of 9 ± 1 pH.

Even at optimum pH, the amount of calcium and/or magnesium in the system has been found to drastically reduce oil recovery and increase contaminants in the froth. Addition of complexing agents for these deleterious ions, particularly sodium tripolyphosphate, will restore good processability. Sodium tripolyphosphate was found to be a better agent than disodium ethylenediaminetetraacetate in these studies.

It has been shown that the more clay (325-fines) in the system, or conversely the lower the oil content, then the poorer the processability of the tar sands. Tar sands that are lower in oil than 6% will presumably be discarded in a commercial mining operation. However, selective, horizontally scraper operations to minimize fines in the mined tar sand feed, by discarding clay strata and lenses, could significantly improve oil recoveries in primary separation. Another important aspect of mining will be to minimize oxidation by immediate use and by avoiding the working a tar sand.

Data obtained to date is not sufficient to draw a general empirical correlation covering all cases. Oil sand grade, clay content, and water phrase pH appear to correlate generally with bitumen recovery and product quality, but there are other factors that can significantly affect oil sand separation. Further, the results of these small scale separations need to be verified in even larger scale equipment than the pilot bench unit and on a range of oil sand types that would be encountered in commercial operation.

However, the laboratory technique for measuring processability of tar sands that has been developed, appears to be a useful research tool for studying most of the process variables of the hot water flotation process. Some of the findings mostly from separations without caustic are summarized below. However variations in tar sand feed quality are probably the most significant variable contributing to differences in results of separations, and caustic addtion can effect improvements up to an optimum condition for separation.

(a) Water Addition

- Froth quality and oil recoveries are not significantly affected by changes of water in mixing over a wide range, i.e. , 15-60 wt %, on good quality tar sand.
- Lowering the water below about 15% in slurrying results in poor separation with no improvement in oil recovery using gentle mixing. This is contrary to the findings of Dr. K. A. Clark working with Bitumount tar sand.
- Higher total water in separation 160 vs 80 wt % on tar sands gave both small increases in both oil recovery and froth quality.

(b) Mixing

- Increasing mixing intensity and to a lesser extent mixing time, increased the water and solid content of the froth and also the oil recovery.
- Mixing tar sand with cold water for extended periods of time appears to have no detrimental effect and perhaps slight beneficial effects on subsequent separation. Hence hydraulic transportation of tar sands should not be harmful to separation.

(c) Aeration

- For the same equivalent total air volume, higher air rates for short periods are more effective for attaining high recoveries of good quality froth than low air rates for longer times.
- Multiple staged skimming can achieve very high oil recoveries from tar sands. The approach was subsequently adopted by CSA in their bench unit.
- Oil recoveries have been found to increase linearly with the log of the air rate used in brass pot lab extractions.
- High air rates, in general, result in a high solid content (or solids/oil ratio) in the froth.
- The above observations suggest that both oil recovery and froth quality can be optimized by separating the oil from the tar sands in a number of cells arranged in series. Very gentle agitation with little or no aeration should be used in the first cell, with increasingly severe conditions in successive cells. This has been tried successfully in the CSA Bench Unit operations.
- Stripping the separated sand phase with air is beneficial for good oil recovery.

(d) Temperature

- Essentially no effect of temperature on oil recovery in the range of 120-190°F has been found with a number of good and poorer quality tar sand provided aeration is used.
- Higher temperature operations appear to give slightly less solids in the froth but water content tends to increase, i.e. , emulsification of oil and water can be reduced directionally by operating at lower temperatures. This is supported by interfacial tension data.
- The small effect of temperature suggests that it may be possible to operate large scale plants at lower temperatures of 130-150°F than the conventional 180°F, just as successfully. This is particularly true if froth can be upgraded in subsequent process operations.
- The same temperature effect was subsequently demonstrated in Bench Unit studies.

(e) Processability of Tar Sands

- Oil recovery is a function of the "naturally occurring pH" of the tar sand.

(i) Neutral to alkaline tar sands give high oil recoveries and good

froth quality.

(ii) Neutral to acidic tar sands give low oil recoveries and poor oil

froth quality.

- Froth quality correlates with fines (325-) content of the tar sands, and hence the concentration of fines in the water phase.
- Oil content of tar sand together with fines content and pH have been found to be the three primary correlating variables with processability.
- Development of a more refined correlation may enable the prediction of separation results from tar sand inspection data.
- Laboratory extraction data on oil recovery correlates generally with results obtained in the bench unit on similar tar sands.
- Laboratory extraction data on froth quality shows the same general pattern as results obtained in the bench unit correlated on the basis of oil content of tar sands.
- The froth from the bench unit contains significantly more water and very slightly less solids on a percentage basis. This may result from either higher mixing intensity or relatively longer mixing times in the Bench unit.
- The highest oil recovery and best froth quality were obtained at an optimum pH for a given tar sand. Although laboratory standard extraction conditions are not necessarily optimum.
- The optimum pH of the separation water phase was found to be about 9 and varied slightly (± 1 pH) with different tar sands and with different additives.

(f) Some Optimum Conditions for Separation

- Separations in the pH range of 8-10 result in high oil recovery in the froth, which has low water and solids content. This pH condition also corresponds to maxima for:
  - *(a) dispersion of particles in suspension (highest negative charge or zeta potential)*
  - *(b) polyvalent ions precipitation.*
  - *(c) dissociation of surfactant carboxylic acid groups (highest negative charge on oil particles).*

and minima for:

  - *(a) contact angle or highest hydration of solid surfaces.*
  - *(b) amount of sodium salt added (notably phosphates and also silicates).*

- The more critical process variables for better physical separations are:
  - *(a) low mixing intensities to effect break down of the tar sand structure in water, and*
  - *(b) staged separation in a series of flotation cells with little or no air addition in the first, and increasing amounts of air, and increasing mixing intensities in subsequent cells.*

7

ADDITIVES

A. Literature Studies

There are few papers on the subject of chemical addition. The more significant processes are briefly summarized below:

Table 7-1

Past Developments in Flotation Processes

				Additives	
	Reported Date	Temperature ^{o}F	Solvent	Inorganic	Organic
Hot Water Process - Clark -	1932	180	-	X	-
Cold Water Process - Montgomery -	1951 1960	70	X (Kerosene)	X	X
Combination Processing - US Bureau of Mines -	1948 1952	180	X (LGO)	X	-

Clark's work was the first of only a few mile stones in the basic work towards an understanding of tar sand separation processing. Apart from hardware development, his main process findings indicated that pH adjustment to within the range of 7-8 was necessary. Sodium carbonate was found to be the best conditioning agent, and the anion played a role, i.e. carbonate was more effect than hydroxide. Further, he recognized that soluble salts of calcium, magnesium or iron must be removed, particularly for tar sands with high salt content, and water washing prior to separation was proposed.

Montgomery used solvents at essentially ambient temperatures to separate the oil from the tar sands. Also studied was the adjustment of pH and addition of surfactants to reduce emulsion formation. Of the surfactants studied, it was found that anionic and nonionic surfactant types were promising. This to some extent agrees with improvements in the froth quality obtained in our hot water flotation studies at Sarnia on addition of combinations of pH controllers (sodium salts of weak acids) and certain types of surfactants.

Using Clark's basic approach, studies of tar sand deposits in the United States were carried out by the U.S. Bureau of Mines. Their findings verified Clark's work. The results of these studies are summarized in Table 7-2. Water washing of the tar sands to remove soluble salts in the case of Edna tar sand was used. Solvent addition to reduce the oil viscosity was also employed in combination with other process operations to achieve the best separation. An aspect of this work was that mild mixing and good pulp dispersion were found to be important for good separation.

B. Inorganic Additives

The effect of the "naturally" occurring pH of the tar sand has been discussed. Different process results can be obtained by adjusting the pH prior to flotation. This section presents studies on the addition of different salts particularly sodium salts of weak acids, on processability. The objective was to define the better inorganic additives to use for oil recovery with poor quality tar sands. In most but not all these experiments, a glass lined sleeve, and a suited glass air disperser was used to minimize interaction of added chemicals with the pot.

7-1 Original Beaker Studies

Essentially, the same result was obtained when using distilled water instead of tap water in hot water flotation separation of a tar sand from Area D, Table 7-3.

The addition of a 0.2 wt% solution of sodium tripoly phosphate (a water softener capable of removing calcium commonly present in water, as a complexed ion) gave only a very small improvement. At a higher concentration of 2.0 wt%, a significant effect was obtained with this sample of tar sands. This supports the concept that removal of certain polyvalent ions has importance in separation, but relatively large amounts of chemicals are needed.

If a pH condition is operative, an improvement would be expected with the addition of a solution of sodium silicate, which is strongly alkaline owing to hydrolysis, under the conditons of separations. This is verified by the data of relatively low concentration. Hence, sodium silicates effective in pH control and tying up polyvalent ions presumably as silicates.

To test the possibility that polyvalent ion removal from solution is the mechanism of improved separation, experiments were carried out with solutions of versene (disodium ethylenediaminetetraacetate). The reason for using such a sophisticated material was its well known ability to inactivate even trace quantities of ions, e.g. Ca^{++} (by forming chelate-type complexes). The versene selected was acidic (pH = 4.3). Efficient complexing of most common metal ions is achieved at pH's higher than 2.0 to 3.5, with the most effective condition being an alkaline solution. The processability of an Area D tar sand with this solution is shown in Table 7-4. The result was significantly poorer than when the tetra-sodium salt formed by sodium hydroxide addition (pH = 9.2) was used. It is interesting that when versene alone was used, the pH of the water phase after separation had increased to 7.0, presumably the versene did react to form complexes, but the pH condition was still too acid to give improved oil recoveries.

Table 7-2

Summary of Small Scale Laboratory Hot Water Flotation Studies of American Oil Sands by U.S Bureau of Mines

Source of Oil **Utah**	**Vernal** **Utah**	**Sunnyside** **California**	**Edna**
Reserve (Total) Million of Barrels	1,150	730	140
Quality of Oil Sand			
Texture	Soft	Hard	Soft
Content, Average Wt%			
Oil (gallons/ton)	12 (29)	9 (21)	11 (26)
Water	1	1	2
Clay	2	13	6
Soluble Salts	No	No	Yes
Oil Inspections			
Gravity, °API at 60°F	8.6	6.7	10
Sulphur, Wt%	0.4	0.5	3.2
Hot Water Flotation			
Process Conditions			
Crushing	No	Yes	No
Water Washing	No	No	Yes
pH Control at 8	No	No	Yes
Sod Carbonate (lbs/ton)	-	-	2.5
Sod Silicate (lbs/ton)	-	-	4.4
Aeration	Yes	Yes	No
Results			
Oil Recovery, Wt%	>90	87	95
Froth Composition, Wt%			
Water	8	17	21
Solids	38	42	6
Oil	54	41	73
Combination Processing			
Process Conditions			
Crushing	No	Yes	No
Water Washing	No	No	Yes
pH Control at 8	Yes	Yes	Yes
Sod Carbonate (lbs/ton)	-	-	2.5
Sod Silicate (lbs/ton0	2	2	4.4
Diluent (L.G.O. - gallons/ton) in			
Mixing With pH Additive	8		
Froth Dilution and Settling	62	62	3.4
Results			
Oil Recovery, Wt%	96	94	96
Product Contamination, Wt%			
Water	0.6	0.8	0.6
Solids	0.5	0.7	0.6
Diluent Loss to Tailings (gallons/ton)	0.1	0.3	0.1

The addition of excess of sodium tripolyphosphate resulted in an improvement at a pH of 9.2. The addition of a surfactant, sodium stearate, at a lower concentration also gave a similar effect. These data show clearly that a significant improvement in oil recovery from poorer (acid) quality tar sands can be obtained by controlling both the pH of the separating water phase at values greater than about 8.0. and using complexing chemistry to sequester deleterious polyvalent ions in the water phase and presumably adsorbed on the surface of solids.

This conclusion may be due to some extent to the fact that alkaline solution is more effective than water in "wetting" solids. This is substantiated by the general decrease in oil content of the sand with increasing pH. This applies to a lesser degree to the solids associated with oil, indicated by a decrease in solids to oil content of the froth with additives.

7-2 Reducing Agents

It was postulated that if an oil sands sample had been "oxidized" then a reducing system might reverse the effect. Froth quality from stannous chloride (reducing agent) treatment of a Hole 11 tar sand prior to separation with sodium hydroxide is shown in Figure 7-5. The effect of increasing pH was to drastically decrease the solids to oil ratio. The oil recovery in these experiments was not significantly improved over the blank experiment with no additives.

The solid to oil ratio of all the experiments carried out with this tar sand in the study is plotted as a function of pH at the bottom of Figure 7-5. It can be seen that at about the optimum pH of 9 the effectiveness of additives in reducing the solids/oil ratio decreased in the order stannous chloride (cold pretreatment), oxalic acid and hydroxylamine hydroxide. This substantiates

Table 7-3

Effect of Salts in Hot Water Separation (Tar Sand from Area "D" contained 9.5% Water, 9.75% Oil and 80.75% Solids)

Water Addition	Tap	Distilled			
Plus		--	0.2% STPP(1)	2.0% STPP(1)	1.0% Sod. Silicate
pH	8.1	(7.0)(2)	--	(9.0)(2)	9.9
Froth Composition, Wt %					
Water	31.1	31.6	20.7	24.7	14.9
Solids	14.3	11.8	8.1	8.6	9.7
Oil	54.6	56.6	71.2	66.7	75.4
Solids to Oil Ratio in Froth	2.6	2.1	1.1	1.3	1.3
Yields, Wt % (water free basis)					
Froth	7.6	7.2	7.1	9.5	9.9
Sludge	13.1	11.8	12.2	13.0	9.0
Sand	79.3	81.0	80.7	77.6	81.1
Oil Recoveries, Wt % (Output)					
Froth	56.9	54.5	57.2	80.9	80.7
Sludge	36.6	38.1	38.7	17.8	16.7
Sand	6.5	7.4	4.1	1.3	2.6
Oil Recovery in Oil Phase, Wt % (Input)	56.0	55.0	58.1	77.7	83.5

(1) Sodium Tripolyphosphate.
(2) Assumed based on other solution measurements.

Table 7-4

Effect of pH in Hot Water Separation (Tar Sand from Area "D" contained 3.4% Water 11.9% Oil and 84.7% Solids)

Solution Addition	**Versene(1)**	**--**	**Versene(1) + NaOH**	**STPP(2)**	**Sod.Stearate**
Concentration in Water, Wt %	0.5	--	0.5	2.5	0.5
pH	4.3	8.1	9.2	9.2	11.3
Froth Composition, Wt %					
Water	22.2	31.3	19.0	23.0	18.3
Solids	6.8	7.8	5.6	5.6	8.5
Oil	71.0	60.9	75.4	71.4	73.3
Solids to Oil Ratio in Froth	0.96	1.28	0.74	0.78	1.16
Yields, Wt % (water free basis)					
Froth	10.0	10.0	11.1	11.2	11.4
Sludge	8.2	7.4	7.3	8.4	9.2
Sand	81.8	82.6	81.6	80.4	79.4
Oil Recoveries, Wt % (Input)					
Froth	74.1	81.4	83.3	85.3	83.0
Sludge	24.0	16.3(3)	15.0	13.4	16.3
Sand	1.9	2.3	1.7	1.3	0.7
Oil in Oil Phase, Wt % (Output)	74.0	70.7	83.7	85.8	82.3
pH of Water-Clay-Sludge Phase	7.0	7.6	7.8	9.1	9.7

(1) Sodium ethylenediaminetetraacetate.
(2) Sodium Tripolyphosphate.
(3) Oil balance does not check, error generally in ash analysis on decanted water phase.

previous findings and that reducing agents may be effective in solids reduction in the froth provided a satisfactory system can be achieved to attain high oil recovery.

7-3 A Lean Hole 11 Tar Sand

A brief preliminary study was carried out under standard conditions in the pot extraction apparatus using a 2 wt% additive solution in mixing. This was equivalent to 11.6 pounds of additive per lb of Tar Sands. A variety of additives were chosen to cover a wide range of pH. A poor quality lean tar sand, from the Hole 11 area containing 7.8 wt% oil, which had a pH of 5.6, was selected as feed.

The oil recoveries are plotted in Figure 7-6 against the pH of the solution added in mixing and the pH of the separated water phase, respectively. In acidic media, oil recoveries were poor. Under alkaline conditions, oil recoveries improved, passing through a maximum when the separated phase had a pH of about 9. The scatter in the data may reflect differences in activity of the additives and/or errors in experimentation. This general treatment, however, showed a similar shaped curve to that found with tar sands of different pH values. Although the maximum oil recovery was only about 80 wt%, this is a significant improvement over the base separation. Presumably, better results might have been obtained with different concentrations of certain other sodium salts, such as phosphate that will be clarified later.

Comparing the plots in Figure 7-6, it is interesting that the curves for the pH of the separated water phase is over a narrower range, most probably due mainly to the buffer action (adsorption) of the clay, Figure 7-7.

The froth composition is plotted in Figure 7-7 and 7-8 against the pH of the solution added in mixing and the separated water phase. It can be seen that in experiments under acid conditions, a very poor froth quality was obtained. However, a very significant improvement was obtained in alkaline media. The oil increased and the solids decreased. Optimum pH appeared to be in the range of ~9.

(a) Emulsion Reversal

Another most important result of practical significance indicated by this study is the change in composition of the froth with salt addition. There is a substantial reduction in water content of the froth with salt addition, which shows a tendency for phase reversal.

This is reminiscent of typical emulsion systems such as a water in oil emulsion stabilized by a sodium soap emulsifier, which may be converted into an oil in water emulsion by the addition of bi or trivalent cations, e.g. Ca^{++}, Fe^{+++}. Addition of Na^{++} ions to equate the effect of the polyvalent cations result in a system, which is neither a water in oil nor an oil in water system. This is not just a valency effect, but the amounts of ions required show that chemical interaction is involved.

If this is a true analogy, the froth must be stabilized by an emulsifier, such as a long chain hydrocarbon with polar groups that occur naturally, e.g. soaps, long chain sulphonic acids and sulphates, and naphthenic acids. All of these produce a considerable decrease in the oil-water interfacial tension.

(b) Summary

These studies have shown that poor processability of a tar sand may be associated with its naturally occurring acidity or salts that are readily hydrolyzed or oxidized producing acids. Control of pH at ~9 indicate substantial improvement and near optimum oil recoveries, cleaner sand, and possibly fewer solids in the froth, from neutralization of acidity, i.e. pH control, by addition of minimum quantities of sodium salts that are either cheap or can be conversely manufactured, e.g. hyroxide carbonate, silicate, etc. Addition of these sodium salts appear to significantly reduce the water content of the froth.

Prewashing of tar sands with water to remove soluble salts prior to mixing and separation does not appear practical for commercial scale operation especially as salt removal from the water will be needed before recycle.

Figure 7-1

Effect of a Reducing Agent (Stannous Chloride) and pH on Froth Quality

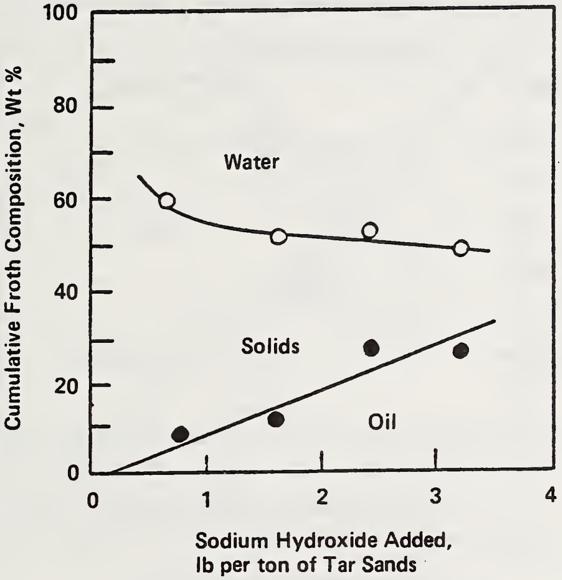


Figure 7-2

Comparison of Solids Reduction in the Froth of Various Agents

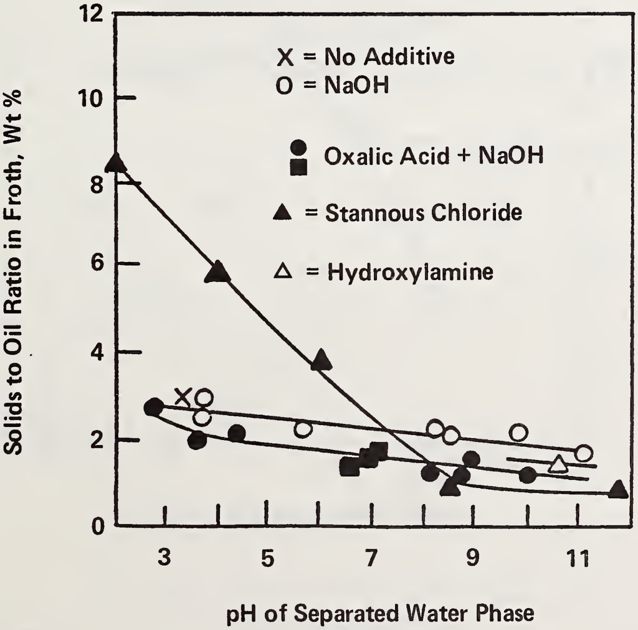


Figure 7-3

Effect of Mixing Solution pH on Oil Recovery (Hole 11 - Lean)

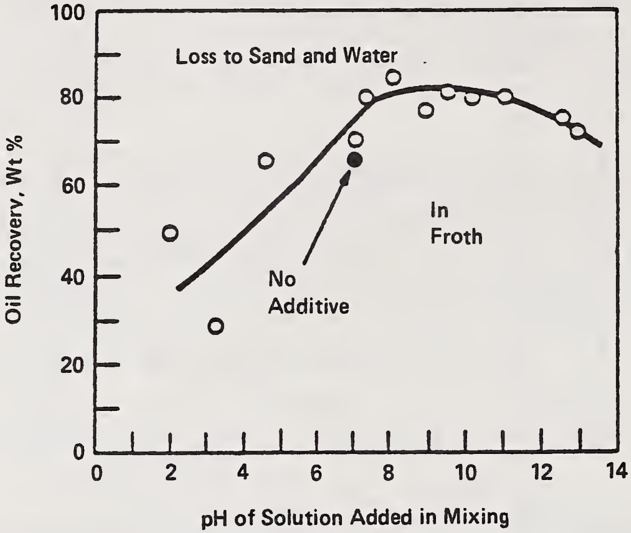


Figure 7-4

Effect of Final pH on Oil Recovery

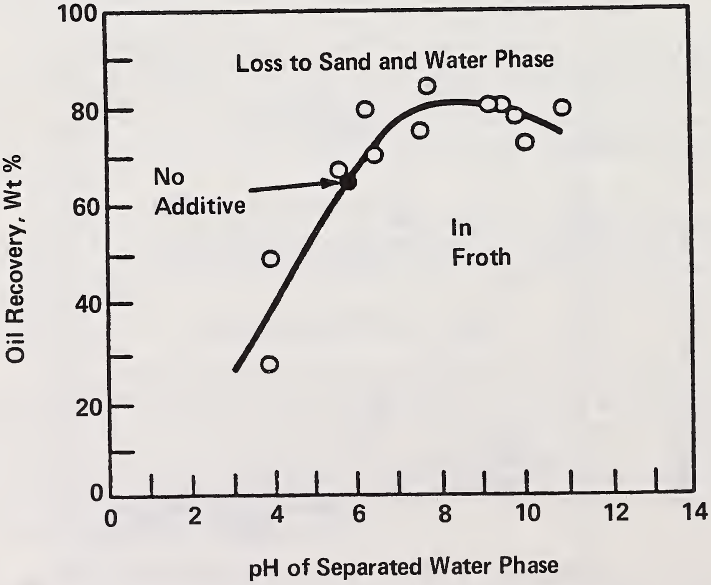


Figure 7-5

Relation of Final and Mixing Solution pH's (Hole 11 - Lean)

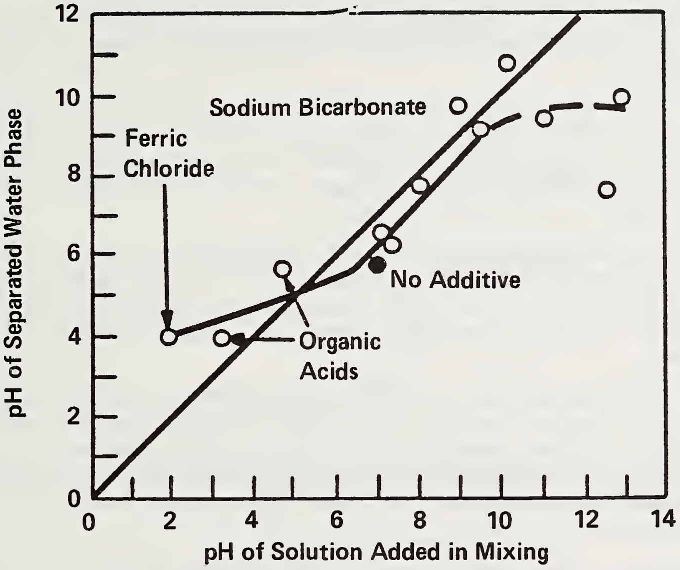
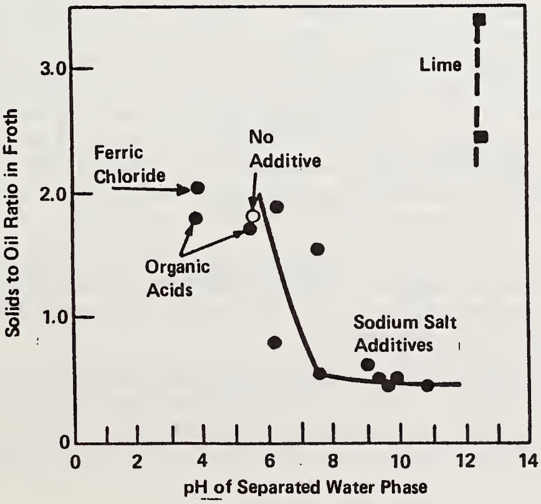


Figure 7-6

Effect of pH on Solids to Oil Ratio in the Froth



7-4 A Rich Hole 11 Tar Sand

A more systematic study of additives was carried out, using a richer tar sand containing 10.8 wt% oil from the Hole 11 area. The additives were essentially sodium salts and all the solutions contained the same amount of sodium, i.e. 0.09 wt% Na on tar sands. It was thought that this approach would show any peculiar effects of the anion. Additives were selected to give a wide range of pH's. This was based on the hydrolysis of the sodium salts, e.g. if HX was a weak acid, an alkaline solution was obtained; however, when HX was a strong acid an acid solution could result.

The oil recoveries are plotted in Figure 7-9 against the pH of the solution added in mixing and the pH of the separated water phase, respectively. It can be seen that the results are similar to the previous study. Optimum pH appeared to be about 9 in the separated water phase. Here, a high oil recovery was obtained, particularly through the use of sodium phosphates added at the rate of about 5.5 pounds per ton of tar sands.

The froth quality is plotted, as before in Figure 7-10. It can be seen that again a significant froth quality improvement was obtained with increasing pH. Although there is a substantial reduction in water content, it will be noted that the amount of solids in froth only decreases slightly with improved conditions. Optimum pH appeared to be about 9 in the separated water phase.

The buffer action of the system is shown by the pH plot in Figure 7-11. Also the decrease in the solids to oil ratio with increasing pH is shown. Two experiments with lime addition were carried out, but a lower concentration than used in the previous study with a lean Hole 11 tar sands, see Figure 7-7. The results again were poor. The behaviour of sodium bicarbonate appeared to be anomalous. It should be noted that sodium sulphide attacks brass, so that any reaction, may affect these data.

7-5 A Low Oil-High Clay Tar Sand

Probably one of the most difficult tar sands to separate is Hole 21A that contains 5.4 wt% oil, 7.2 wt% water, 31.5 wt% 200 fines and 55.9 wt% sand. It has been found in earlier studies that significant improvements in processability can be achieved with addition of sodium tripolyphosphate. A study was, therefore, undertaken using a number of sodium salts, which had proved to be effective with Hole 11 tar sands. The concentration of these additives were varied in these experiments.

Oil recoveries and froth compositions for separations with sodium carbonate, sulphide and hydroxide are plotted against the amount of additive used in Figure 7-12. The pH's of the separated water phases are shown numerically besides the points. The results are not spectacular.

Oil recoveries and froth qualities with sodium tripolyphosphate and silicate are compared with hydroxide in Figure 7-13. It can be seen that oil recoveries of about 80 wt% were obtained with the two salts at low addition levels of 2.3 and 2.9 pounds per ton of tar sands. The fact that both tripolyphosphate and silicate gave better results than hydroxide at the same sodium content of 0.045 wt% on tar sands suggests that these anions have some action in the process. High concentrations of silicate accompanied by a higher pH of 9.0 caused a decrease in oil recovery which may have been due to deposition of silica on solids and oil, causing loss of oil to the water phase. This is substantiated by experimental difficulties when working with sodium silicate, in that filter plugging occurs probably due to deposition of silica.

The low pH range of 6.8-7.3 for all concentrations of sodium tripolyphosphate indicates strong reaction or adsorption. It should be pointed out that adsorption of phosphates by clay is a well-known phenomena. Best results were obtained with sodium tripolyphosphate at the highest concentration used in this study.

Froth quality has been plotted against amounts of additive in Figure 7-13. It can be seen that the froth quality from extractions with tripolyphosphate, silicate and hydroxide are the same at all levels of addition, except for the hydroxides at the highest concentration. Increasing the amount of additive clearly shows a substantial improvement in froth quality.

Figure 7-7

Effect of Mixing Solution pH on Oil Recovery (Hole 11 - Rich)

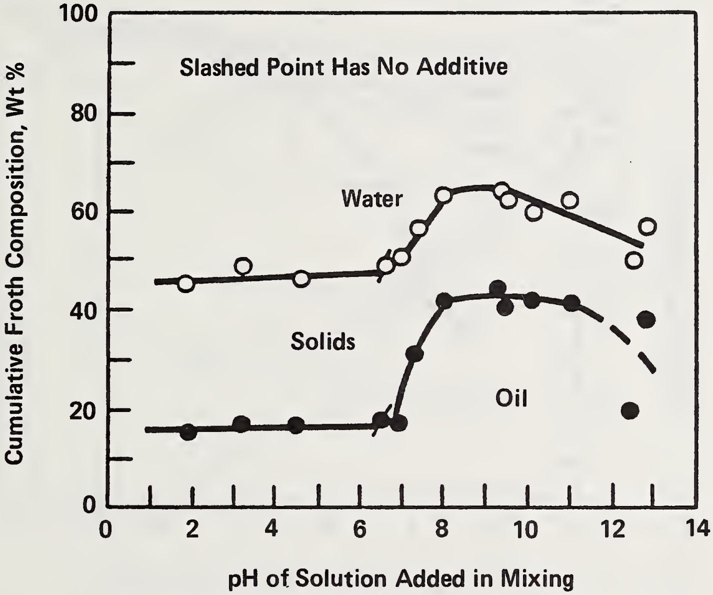


Figure 7-8

Effect of Final pH on Froth Composition

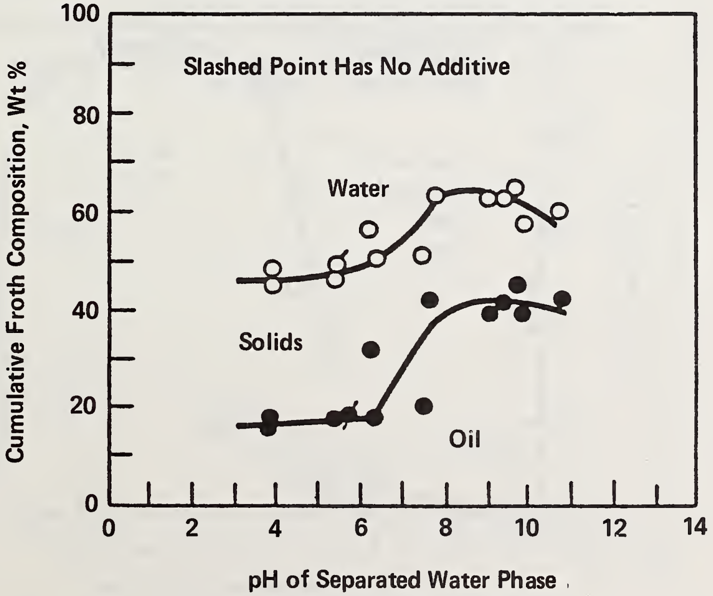


Figure 7-9

Effect of Mixing Solution pH on Froth Composition (Hole 11 - Rich)

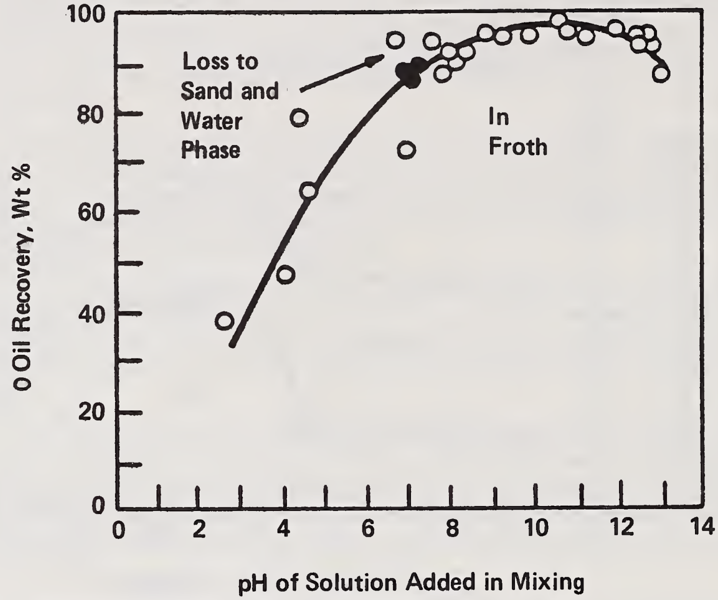


Figure 7-10

Effect of Final pH on Froth Composition

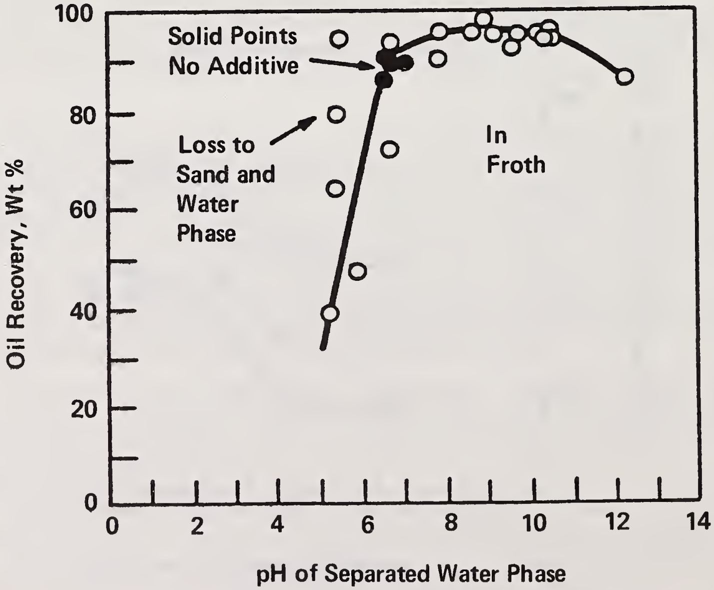
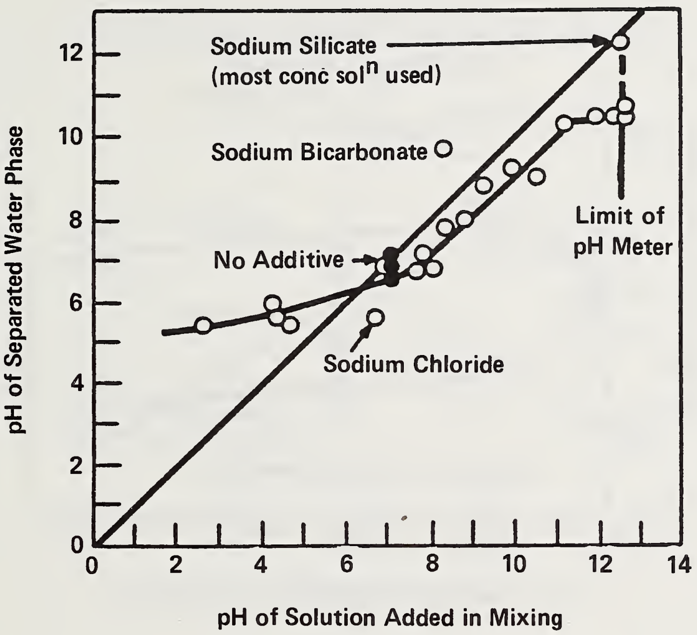


Figure 7-11

Relation of Final and Mixing Solution pH's (Hole 11 - Rich)



EFFECT OF pH ON SOLIDS TO OIL RATIO IN FROTH

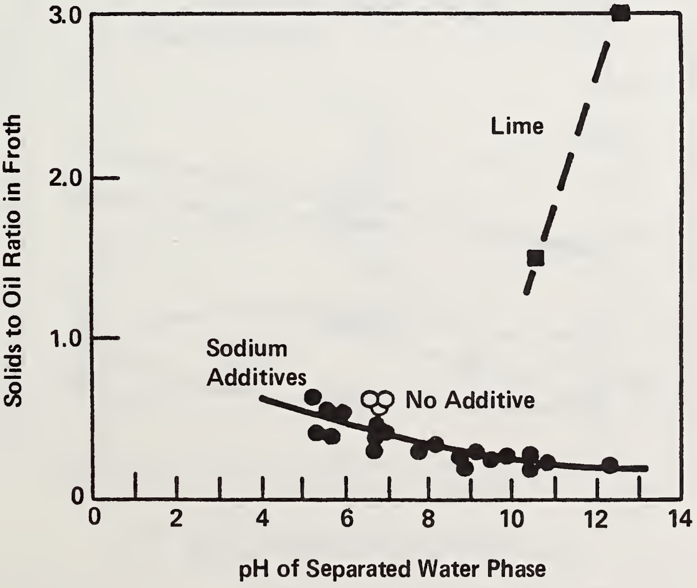
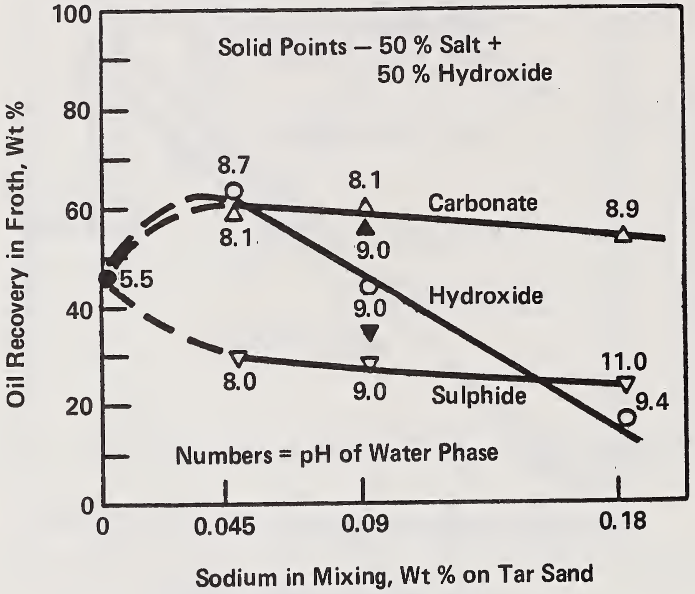


Figure 7-12

Effect of Sodium Salt Concentration on Oil Recovery (Hole 21A)



EFFECT OF SODIUM SALT CONCENTRATION ON FROTH COMPOSITION

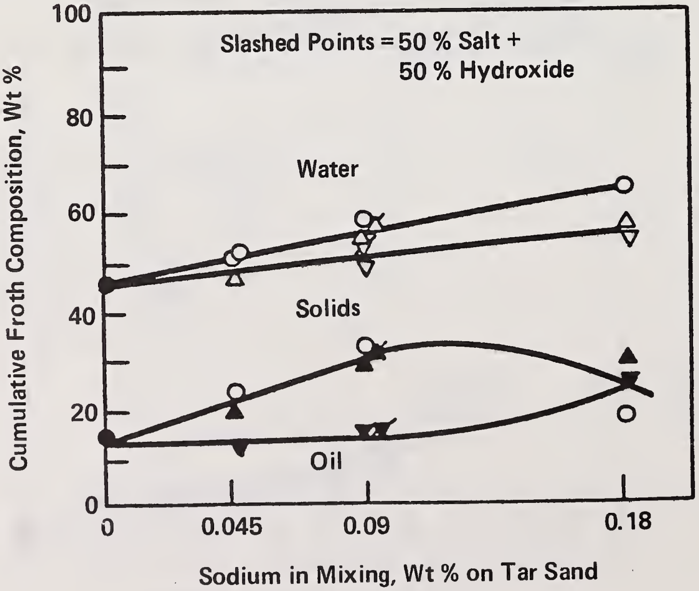
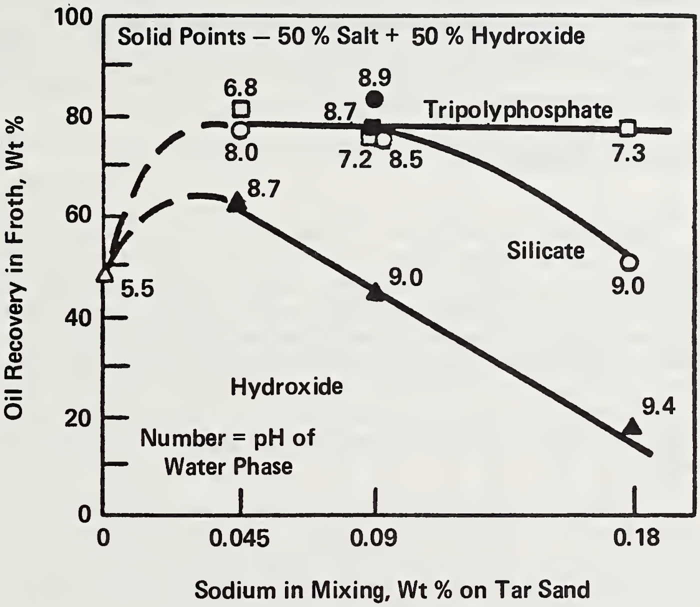
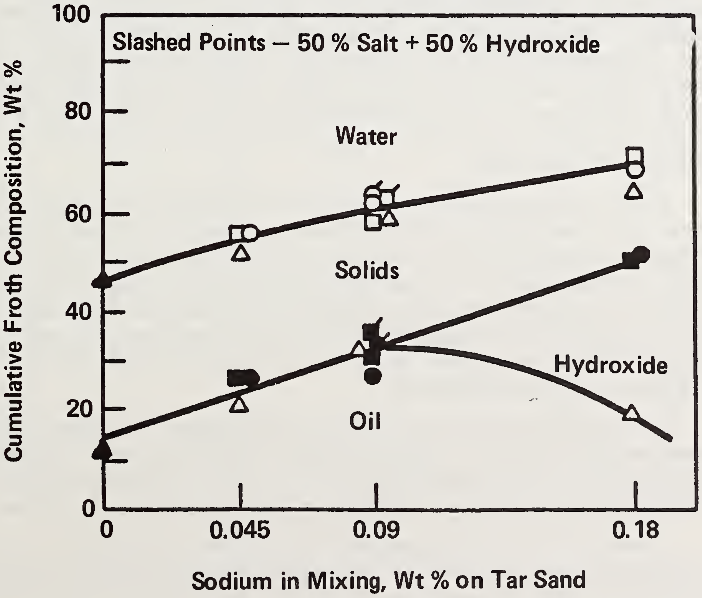


Figure 7-13

Effect of Sodium Salt Concentration on Oil Recovery (Hole 21A)



EFFECT OF SODIUM SALT CONCENTRATION ON FROTH COMPOSITION



7-6 Miscellaneous Tar Sands

Studies with a high oil (14.9%), low water (0.6%), low pH (3.1), tar sand from the National Research Council (Ottawa) showed this sample would not separate in the hot water flotation process. It was originally from the Bitumount Area and had been in storage for some time. Presumably the acid condition and perhaps the low water could have resulted from "aging", i.e. oxidation Fe^{++},Fe^{+++} from exposure to air, at the time of sampling. It should be noted that separated clay suspensions were positively charged indicating adsolved trivalent cations. A number of separations on the small samples available with sodium hydroxide, tripolyphosphate and silicate showed an optimum pH of about 9.

7-7 Silicates and Phosphates

(a) Sodium Silicates

Sodium silicate is used widely in flotation of minerals as a dispersant and depressant for quartz and silicate minerals. There are several forms of sodium silicate which are generally characterized by the ratio of SiO_2:Na_2O. These different forms yield different products by hydrolysis other than sodium, e.g. $H_3SiO_4^-$, $H_2SiO_4^{2-}$, H_2SiO_3 and $HSiO_3^-$. Two reactions are of interest and perhaps significant in hot water flotation of tar sands. Sodium silicate solutions especially with high ratios of SiO_2:Na_2O give colloidal dispersions of silicic acid in aqueous suspensions. Also, ions of heavy metals, e.g. iron, react readily at low concentrations to form amorphous precipitates of hydrated mixed oxides of unknown structure. Since improved processability has already been shown for sodium silicate addition, a study of different silicates was carried out.

The results of these separations with a Hole 11 tar sand and sodium silicate addition in mixing is shown in Table 7-5. The ratio of SiO_2:Na_2O was varied from 0.5-3.22, at three levels of sodium content in the mixing solution for each of the four ratios. A general treatment of the data is given in Figure 7-14. The results show a maximum oil recovery at a low sodium concentration. At higher concentrations, the data diverge indicating good oil recoveries with SiO_2:Na_2O ratios of 1.0 and less, and poor oil recoveries at higher ratios. In general, the froths are similar in quality, Figure 7-15.

The oil loss to the sand, Figure 7-15, was reduced with decreasing ratios of SiO_2:Na_2O. pH values on the water phase ranged from 9.7-11.5, and there did not appear to be any correlation except that the system became basic with sodium silicate addition and good results were obtained with this tar sand, Table 7-5. One experiment recorded in this table was conducted with a low concentration of sodium tripolyphosphate. The pH was 7.8, and the oil recovery of 95.1% was the highest and the sand was the cleanest of all the experiments. However, the froth contained slightly more water and less oil than those from the separations using sodium silicate. Again, this shows that sodium tripoly phosphate appears better than silicate in overcoming the attachment of oil to solids.

The lower plot in Figure 7-15 shows that only low silicate concentrations of less than 1 wt% on tar sands gave good oil recovery. There is some scatter in the data indicating that different silicates give slightly different results. The best results found for low SiO_2:Na_2O ratios of <1.0 appear to be contrary to the normal use of sodium silicates mineral in flotation, of 2.2 and 3.0. However, it should be realized that hydrolysis and hence more free hydroxide occurs both with increased dilution and increased temperature. As the temperature was the same in all the experiments, 180°F, the maximum in Figure 7-14 is probably due to the effect of dilution of sodium silicate with high SiO_2:Na_2O ratios.

It is interesting to note that with higher concentrations of sodium silicate in aqueous solutions, the silicic acid from hydrolysis exists in colloidal forms, i.e. micelles. The reduced oil recovery at higher silicates could result from a colloidal phenomena at the surface of oil particles rendering them hydrophilic (and hydrated) and hence excluding air attachment.

It may be tentatively concluded that sodium silicates with low SiO_2:Na_2O ratios of about 1.0 or less appears to be more desirable for the separation of oil from solids. Their use would avoid definition of critical concentrations of sodium silicate of higher SiO_2:Na_2O ratios, that is similar

Table 7-5

Effect of Sodium Silicate of Different $Na_2O:SiO_2$ Ratios but Equivalent Sodium Content on a Hole 11 Tar Sand

Sodium Additives*	-	"G" Silicate			"G" Silicate			Metso Anhydrous			--------"200"---------				NaTPP**
Moduli: SiO_2/Na_2O	-	--------3.22------			---------2.0------			---------1.0--------			-----------0.5-----------				-
Sodium in Mixing Sol^n Wt % on Tar Sand	-	0.045	0.090	0.135	0.045	0.090	0.135	0.045	0.090	0.135	0.028	0.045	0.090	0.135	0.045
Silica in Mixing Sol^n Wt % on Tar Sand	-	0.195	0.391	0.586	0.122	0.243	0.365	0.061	0.122	0.165	0.015	0.030	0.061	0.091	-
lbs Sodium Salt (Anhydrous) per Ton of Tar Sands	-	5.34	10.70	16.56	3.78	7.56	11.32	2.34	4.66	7.00	0.93	1.87	3.74	5.61	2.90
Results, Wt %															
Froth Composition															
Water	45.0	26.9	22.3	24.1	21.8	22.4	27.5	27.2	26.1	29.9	30.3	25.2	28.8	30.4	38.1
Solids	19.1	13.9	10.5	9.8	10.3	11.1	8.9	12.0	12.5	10.1	17.7	11.2	11.6	10.3	14.3
Oil	35.9	59.2	67.2	66.1	67.9	66.6	63.7	60.8	61.4	60.0	52.0	63.7	59.6	59.2	47.6
Solids/Oil Ratio	0.53	0.23	0.16	0.15	0.15	0.17	0.14	0.20	0.20	0.17	0.34	0.18	0.20	0.18	0.30
Yields (Dry Basis)															
Froth	13.5	13.1	10.7	8.9	11.6	10.8	9.2	12.1	11.6	11.4	13.7	11.9	11.4	11.8	13.8
Water Phase	3.9	3.4	5.2	6.9	4.1	5.7	6.3	4.4	4.8	5.1	4.1	5.0	4.6	4.7	4.4
Sand	82.6	83.4	84.0	84.2	84.3	83.5	84.4	83.5	83.6	83.5	82.1	83.1	84.0	83.5	81.7
Oil Recovery															
Froth	81.7	93.6	86.2	75.1	91.6	84.5	77.2	91.5	88.2	90.0	91.5	91.1	90.0	90.3	95.1
Water Phase	9.8	5.4	11.5	22.8	7.0	14.3	20.4	7.7	10.9	9.2	5.5	8.7	9.5	9.1	4.9
Sand	8.5	1.0	2.3	2.1	1.4	1.2	2.4	0.8	0.9	0.8	3.0	0.2	0.5	0.5	0.0
Tar Sand Comp^n (Cal^c)															
Oil	10.4	10.9	10.4	10.0	10.6	10.6	10.2	10.7	10.5	10.5	10.9	10.7	10.5	10.7	10.8
Water	3.2	4.1	3.0	3.1	3.4	3.1	3.2	3.2	3.3	3.4	3.1	3.4	3.4	3.1	2.5
Fines	7.3	5.1	5.3	5.5	4.6	5.5	5.2	5.4	5.4	5.5	6.8	5.6	4.9	5.3	6.9
Sand	79.1	79.9	81.3	81.4	81.4	80.8	81.5	80.7	80.7	80.5	79.3	80.3	81.2	80.9	79.8
Zeta Potential (mv)	13.7	16.8	18.2	21.0	16.2	20.8	18.3	17.0	21.9	24.2	13.7	16.5	24.4	22.0	-

* Sodium Silicates from National Silicates Ltd.

** Sodium Tripolyphosphate.

Figure 7-14

Effect of Different Silicates on Processability of a Hole 11 Tar Sands

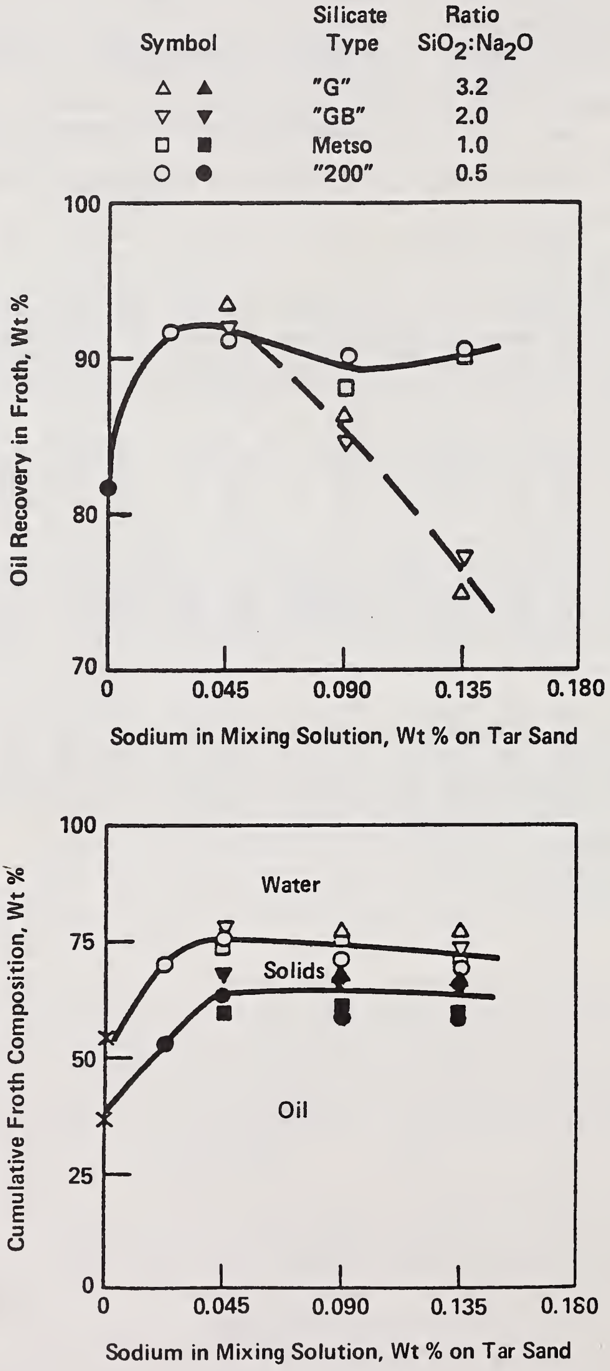
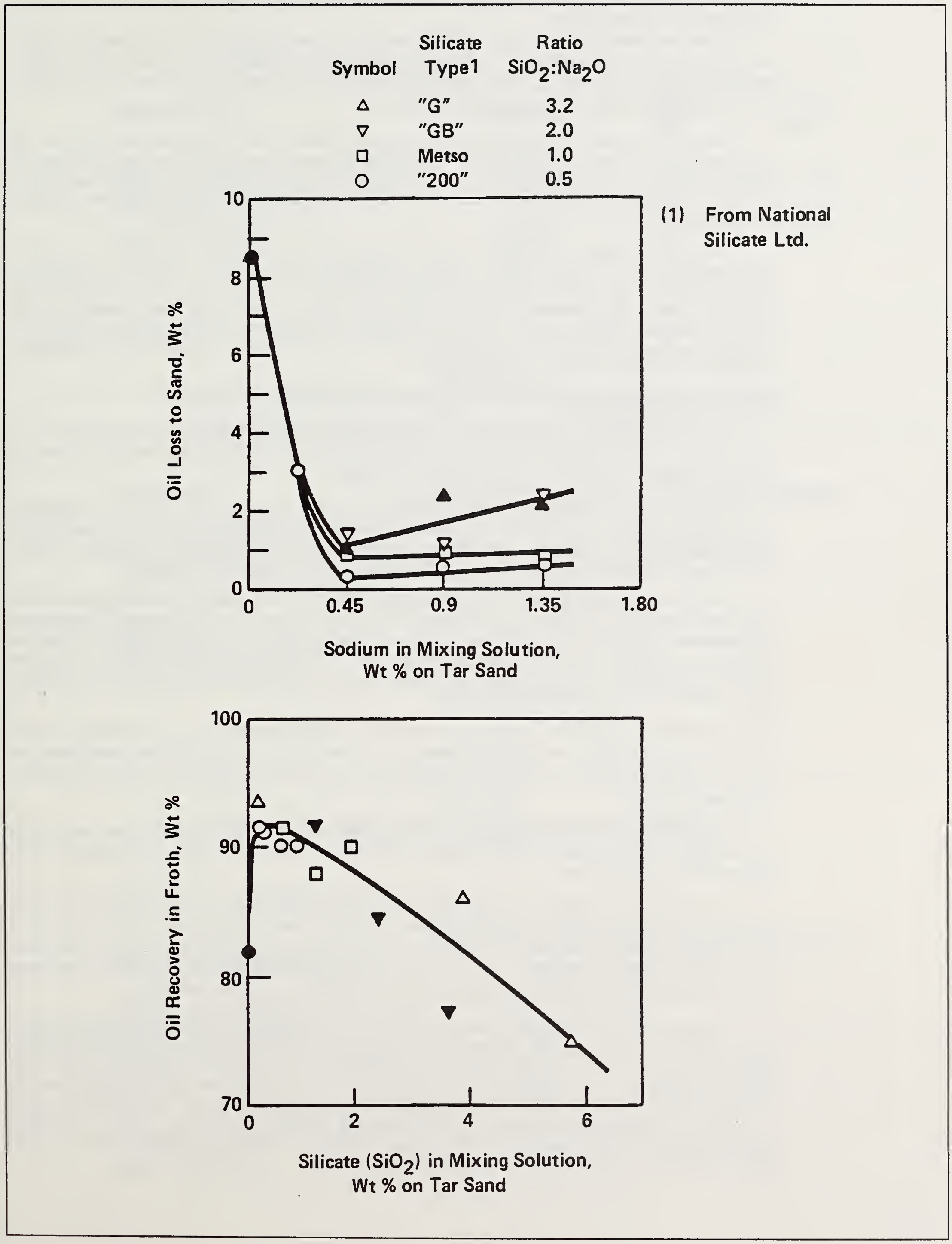


Figure 7-15

Effect of Different Silicates on Processability of a Hole 11 Tar Sands



to caustic soda, see Figure 7-13 and hence not run the risk of oil loss when processing variable quality tar sands.

(b) Sodium Phosphates

A general conclusion, of earlier studies was that sodium phosphates and silicates are better additives than sodium hydroxide. Sodium phosphates are in general better than silicates. Phosphates with low Na:P and O:P ratios, and silicates with low SiO_2:Na_2O ratios are the preferable types from these classes of compounds, Table 7-6.

The relative cost of suitable technical grade silicates and phosphates will have to be developed for economic evaluation. At present, it appears that sodium hydroxide, silicate or fusion product are best for some tar sands but the more selective phosphates will be required for other more critical types, in that these types of polyphosphates are excellent sequestrating agents for polyvalent cations.

Further separations with addition of sodium tripolyphate to a Hole 11 tar sand in (a) mixing, (b) flooding, and (c) after aeration showed substantial benefits over no addition. Addition in mixing and flooding were best and almost equivalent. However, addition after aeration was significantly poorer. This presumably resulted from inadequate agitation and time to reach an equilibrium condition under the test conditions. Addition in mixing is preferred although addition in flooding is also satisfactory. A more detailed study was carried out to measure relative phosphate effects at constant sodium content, Table 7-7

(c) Hole 11 Oil Sand

The tar sand used in this study was originally dug from a Mildred Lake surface hole - C. S. A. I. Hole 10. The sample in a plastic bag was sealed in a can and shipped to Sarnia. The can had been in storage for 2 1/2 years at ambient temperatures.

It was homogenized and sieved just prior to use, which is standard practise. The homogenity of the feed may be in question as other samples of tar sands placed in storage at the same time and undergone some separation with oil pools forming in the bottom of the plastic bags. Further, clay lenses were present in this particular sample, that were difficult to homogenize.

This feed was chosen as it exhibited poor quality and a low pH of 2.7, indicating that oxidation had taken place. Thus, scope would be provided in separation to measure and compare any improvements achieved with different phosphates. Further, the acid (aged) condition of this surface tar sand indicated that deleterious polyvalent ions would probably be present for sequestration, as solubility of polyvalent ions generally increases with decreasing pH, and an adsorption equilibrium would have been established.

Separations were carried out using the standard Brass Pot procedure. As this study was exploratory, ash analyses were used to determine oil associated with solids in the water phase and sand. This technique was considered adequate for this first evaluation of different types of sodium phosphates.

Seven different sodium phosphates at a minimum of three concentrations were used. Additions were made in mixing, distilled water was used in flooding. All mixing solutions were made up just prior to separation.

The effect of different concentrations of sodium phosphates on oil recovery and froth quality is shown in Figure 7-16, and the data are summarized in Appendix Tables. A series of curves are defined for the different phosphates. Condensed or polyphosphates gave better results than sodium salts of phosphoric acid. The preferred order of condensed phosphates indicated from these studies was tripolyphosphate, hexametaphosphate, and pyrophosphate.

In the fall of 1963 Monsanto announced a new type of phosphate (deflocculant) for the detergent field, which was called "Dequest". Two laboratory preparations Dequest 2000 and 2006 were obtained and tried. The results plotted in Figures 7-16 are not impressive. The main disadvantage appeared to be the low pH, when used in hot water separations. Some studies were carried out where Dequest (deflocculant) + sodium hydroxide (pH adjuster) were added. Average results are compared with those for sodium tripolyphosphate following Table 7-8. Sodium tripolyphosphate appeared to be both a better additive in hot water separation and a better deflocculant than Dequest phosphate 2006 in these studies.

Table 7-6

Decreasing Effectiveness of Phosphates for Sequestration of Calcium(45)

Phosphate Type	Formula	Na:P Ratio	O:P Ratio
Sodium Hexametaphosphate (calgon)	$(NaPO_3)_6$	1.0	3.0
Sodium Tripolyphosphate	Na_5P_3O	1.7	3.3
Tetrasodium Pyrophosphate	$Na_4P_2O_7$	2.0	3.5
Sodium Phosphate	Na_3PO_4	3.0	4.0

Table 7-7

Decreasing Effectiveness of Phosphates for Sequestration of Calcium(45)

Sodium Salt	Salt Weight for Equivalent Sodium Sol. Content
Hexametaphosphate	1.38
Tripolyphosphate	1.00
Pyrophosphate	1.51
Phosphate	1.72
Monohydrogen Phosphate	1.81
Dihydrogen Phosphate	1.87

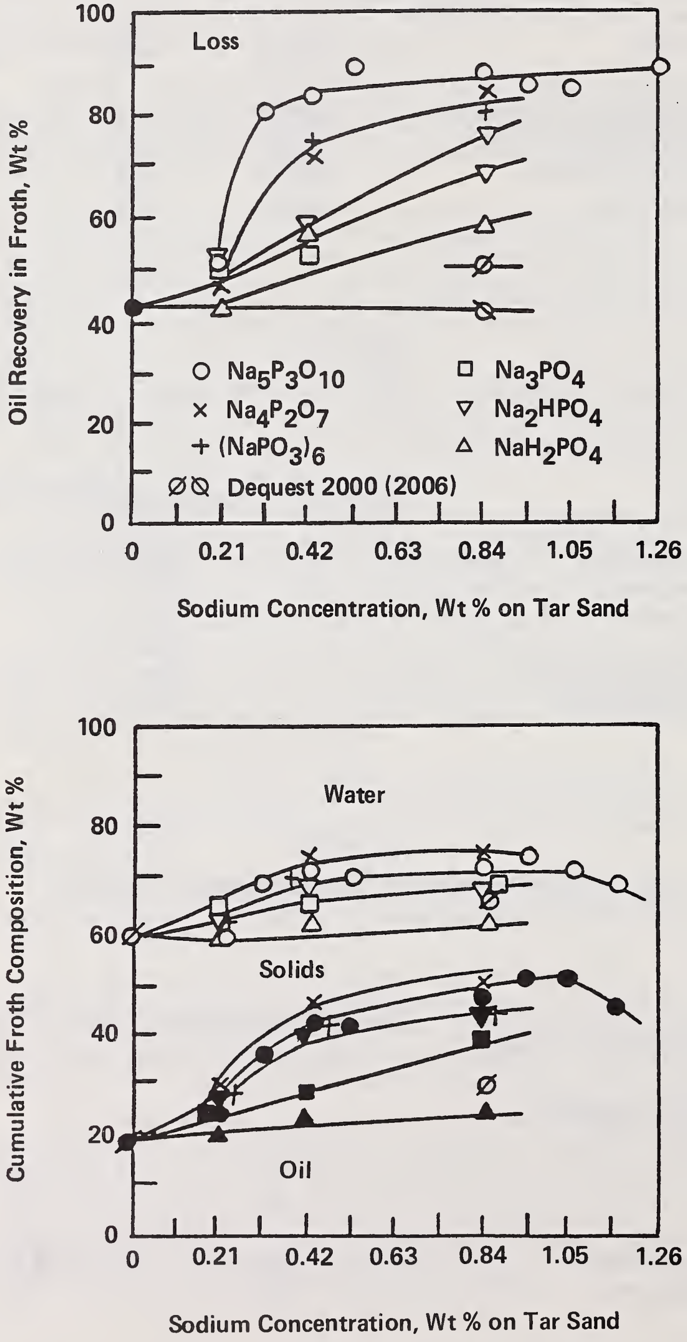
Table 7-8

Sodium Tripolyphosphate is Superior to Dequest Phosphates

	Sodium Tripolyphosphate	Dequest 2006+NaOH
pH of Separated Water Phase	---------------------- 8	---------------------
Froth Composition, Wt%		
Water	28	31
Solids	24	25
Oil	48	44
Oil Recovery, Wt%	85	73
Zeta Potential, mv.	31	27

Figure 7-16

Effect of Sodium Phosphates and Concentration on Processability of a Poor Quality Tar Sand



It appears from either a process or quality advantages, the order of preference (assuming equivalent cost per pound) is sodium tripolyphosphate>hexametaphosphate>pyrophosphate. Sodium phosphate and hydro phosphates are not as good.

(d) pH Effect

Oil recovery and froth quality are plotted in Figure 7-17 as a function of pH. The oil recovery results seem to indicate two general groups. Sodium phosphates that yield phosphoric acid on hydrolysis gave lower values than so-called condensed or polyphosphates. However, the froth quality data gave a single correlation with pH.

The relationship of pH with sodium phosphate type and concentration is shown in Figure 7-18. It can be seen that each sodium phosphate exhibits a characteristic pH, which is almost independent of its concentration, i.e. buffer solution. Increasing phosphate concentration raises the final pH of the separated water phase, which will presumably approach asymptotically the characteristic buffer solution pH. This plot serves to show the quantitative value of the additive in achieving more desirable pH separation conditions. Presumably optimum additives quantities will vary considerably for different tar sands.

In general, sodium phosphate exhibiting buffer solution characteristics in the optimum alkaline pH range of 9 ± 1 appear to work best. The final pH of separation is dependent more on the concentration of the sodium phosphate additive than on the pH of the original solution.

(e) Zeta-Potential Effect

The average zeta potential of particules in the final water phase is plotted in Figure 7-19 against oil recovery and froth quality. The data indicates only a general correlation. The average zeta potential as a function of pH with parameters of different sodium phosphates is shown in Figure 7-20. The peculiar shape of the parameter for sodium tripolyphosphate presumably shows the expected effect of high salt concentrations on zeta potential.

It is interesting to compare average zeta potentials at a constant pH as shown in the following tabulation:

This may be a questionable method of handling the data, but it shows an inverted effect on zeta potential of sodium phosphates from phosphoric acid compared with those derived from polyphosphates with the order shown, which correlates generally with the Na:P ratio.

Table 7-9

Zeta Potentials at Constant pH

Sodium Salt	Formula	P:N Ratio	Av. Zeta Potential mv. at 7 pH
Hexametaphosphate	$(NaPO_3)_6$	1.0	~34
Tripolyphosphate	$Na_5P_3O_{10}$	1.7	32
Pyrophosphate	$Na_4P_2O_7$	2.0	27
Phosphate	Na_3PO_4	3.0	17
Monohydrogen Phosphate	$NaHPO_4$	2.0	21
Dihydrogen Phosphate	NaH_2PO_4	1.0	~30

Of particular note is the property of sodium hexametaphosphate (calgon) to increase zeta potential, that is effect dispersion. It appears to be a better defloculant than sodium tripolyphosphate. The particular pure form used, however, gave a characteristic pH of less than 7.

Zeta potentials of phosphate treated solids show a relationship with pH and hence separation. In general the higher the zeta potential the better the separation. Comparative studies of hexametaphosphate in alkaline media with sodium tripolyphosphate are clearly indicated. A good deal more development work is required to utilize this type of measurement to predict processability. A new approach in which the zeta potential is measured in the original water phase (centrifuged) is being developed. In this technique, measured zeta potential will be substantially higher.

Figure 7-17 (a)

Effect of Sodium Phosphate Additives on Processability as a Function of pH

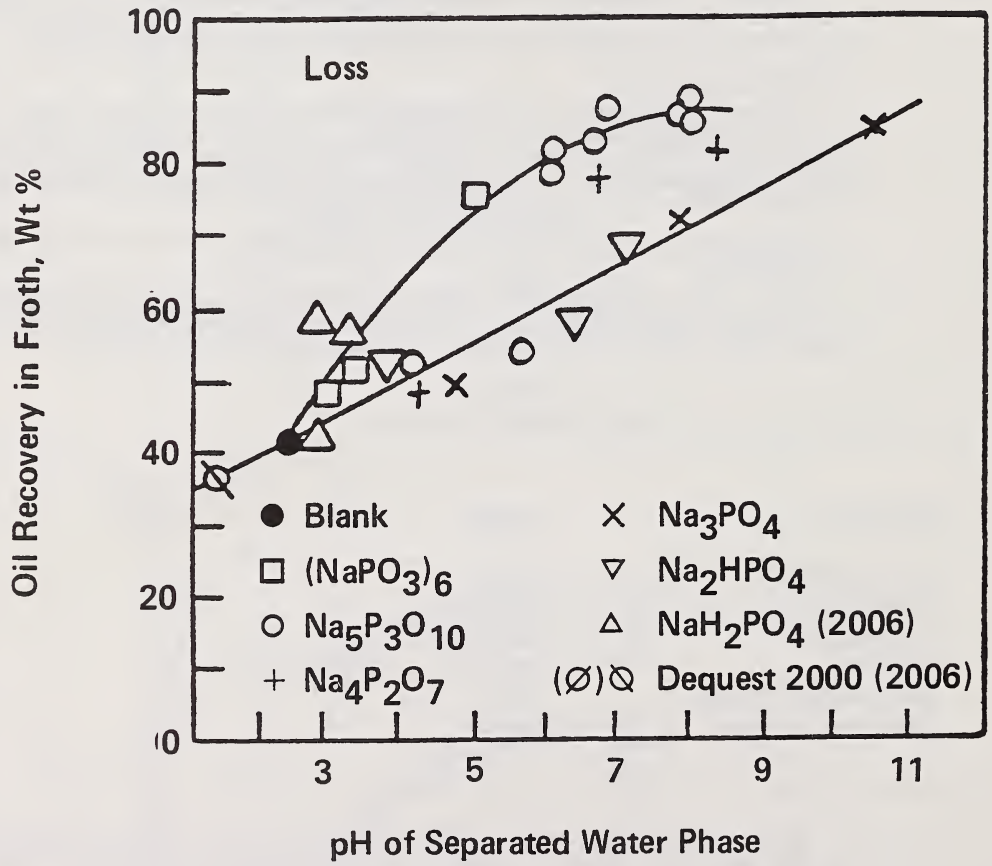


Figure 7-17 (b)

Effect of Sodium Phosphate Additives on Processability as a Function of pH (Continued)

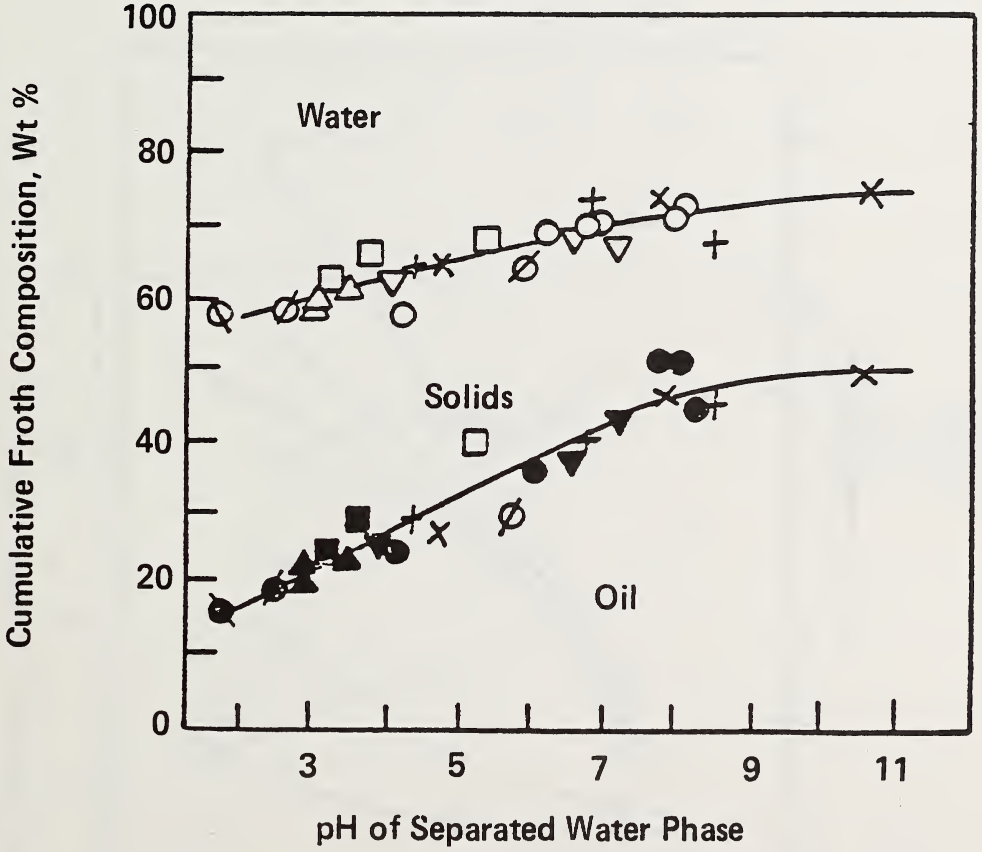
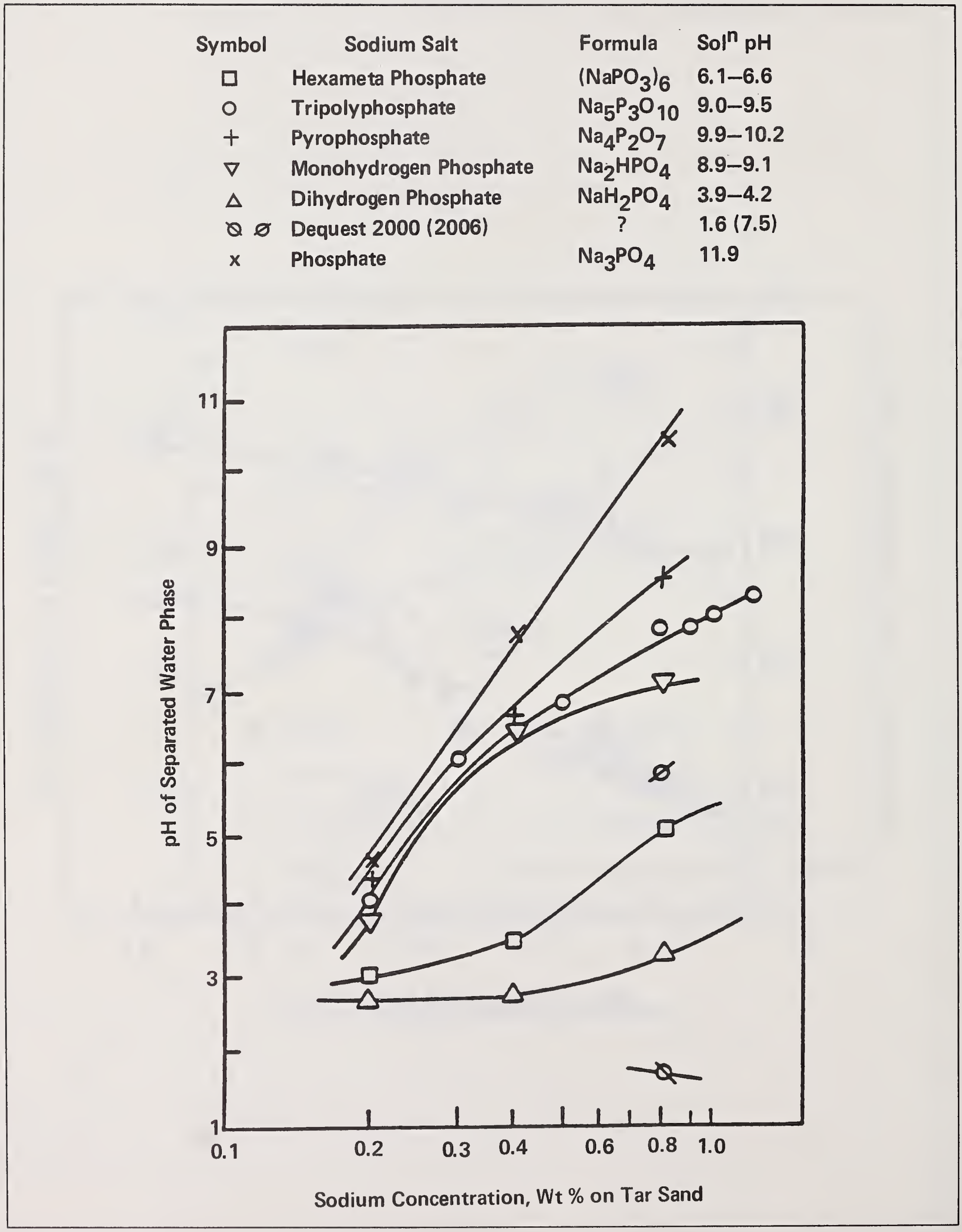


Figure 7-18

Relationship of Sodium Phosphate Additive and Concentration with pH



Symbol	Sodium Salt	Formula	Sol^{n} pH
□	Hexameta Phosphate	$(NaPO_3)_6$	6.1–6.6
○	Tripolyphosphate	$Na_5P_3O_{10}$	9.0–9.5
+	Pyrophosphate	$Na_4P_2O_7$	9.9–10.2
▽	Monohydrogen Phosphate	Na_2HPO_4	8.9–9.1
△	Dihydrogen Phosphate	NaH_2PO_4	3.9–4.2
⊘ ∅	Dequest 2000 (2006)	?	1.6 (7.5)
x	Phosphate	Na_3PO_4	11.9

Figure 7-19

Relationship of Zeta Potential and pH of Water Phase For Different Sodium Phosphate Additives at Different Concentrations

Symbol	Sodium Salt	Formula	Sol^n pH
●	Blank		
□	Hexameta Phosphate	$(NaPO_3)_6$	6.1–6.6
○	Tripolyphosphate	$Na_5P_3O_{10}$	9.0–9.5
+	Pyrophosphate	$Na_4P_2O_7$	9.9–10.2
×	Phosphate	Na_3PO_4	11.9
▽	Monohydrogen Phosphate	Na_2HPO_4	8.9–9.1
△	Dihydrogen Phosphate	NaH_2PO_4	3.9–4.2

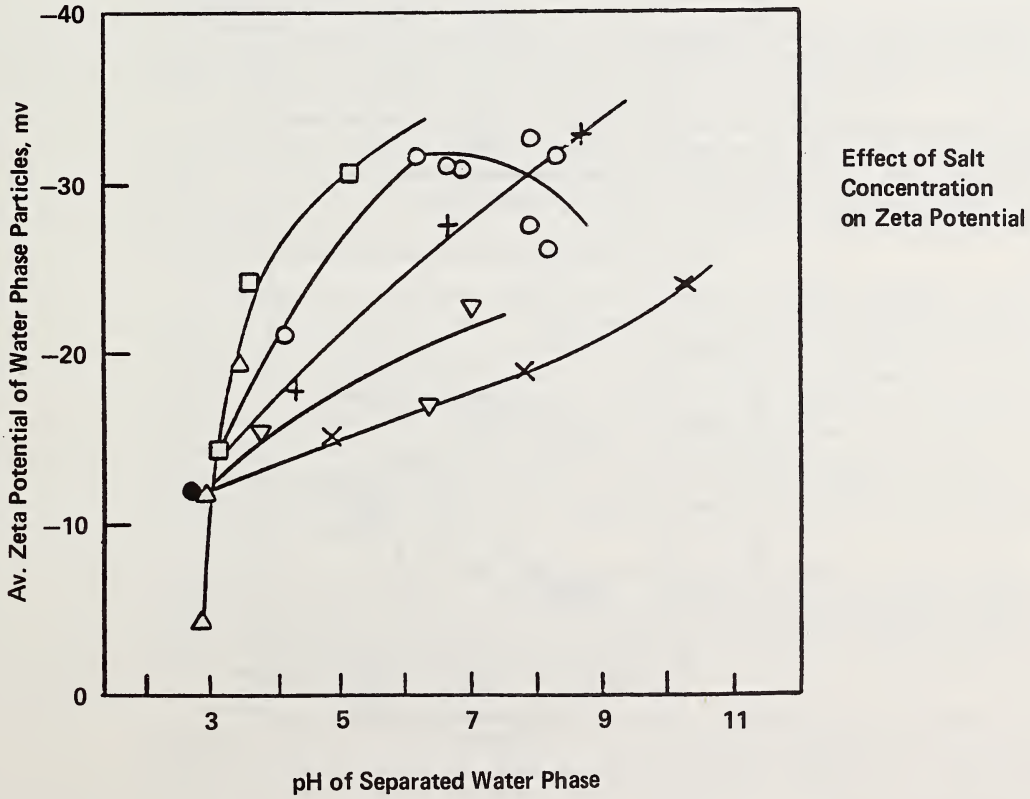
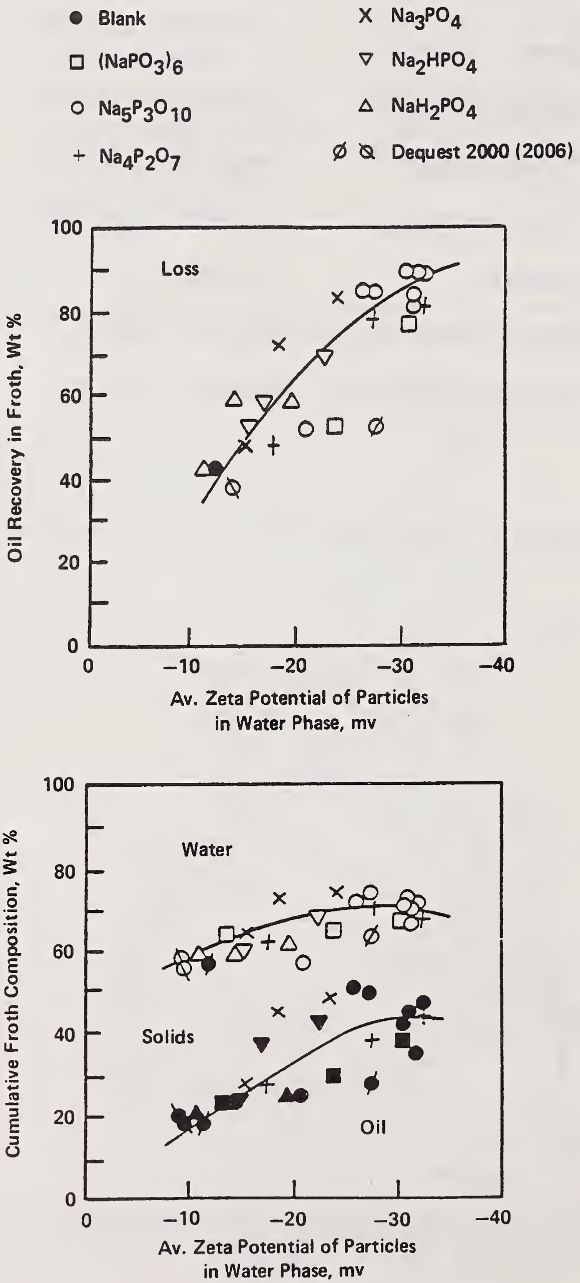


Figure 7-20

Effect of Sodium Phosphate Addition on Processability as a Function of Zeta Potential



7-8 Comparison of Sodium Salts

The results of a few comparative studies with addition of sodium silicate and sodium hydroxide indicated in general poorer results than with sodium tripolyphosphate.

Table 7-10

Comparison of Hydroxide - Silicate - Tripolyphosphate

Sodium Additive	**Hydroxide**	**Silicate "200"**	**Tripolyphosphate**
Froth Composition, Wt%	51	35	30
Water	51	35	30
Solids	29	30	29
Oil	20	35	41
Solids/Oil Ratio	1.5	0.9	0.7
Oil Recovery, Wt%	51	70	82
pH of Separated Phase	11.1	9.8	6.7
Zeta Potential, mv	25	21	31

The comparison shown, is based on equivalent concentrations as not enough experiments were carried out to make a comparison on the basis of an equivalent pH.

(a) A More Comprehensive Study

This study was planned and conducted to obtain an overview of the effects of water phase properties on processability. The whole data therefore have been treated in subsequent plots regardless of the type of additive, and grouped only according to type of tar sand.

The processability of eight different tar sands was measured with and without the addition of alkaline sodium salts. The properties of these tar sands are recorded in Table 6-34. The sodium salts selected for evaluation were hydroxide, carbonate, silicate, and tripolyphosphate. The electrical and chemical parameters associated with these additions are given in Table 6-35. The separation procedure and results in Table 6-36. The results of these experiments with sodium additives are summarized in the Appendix.

Oil recovery in the first froth obtained with no aeration in primary separation in these studies is plotted against pH in Figure 7-21. It will be noted that in all cases high oil recoveries in the order of 85 to 90 wt% were obtained with all types of tar sands, except Beaver River "Bad" tar sand that will be later discussed as a separate item. The data shows that the oil recovery passes through a maximum in the pH region of 8-10 pH. However, processability is still good even at pH's up to 12. In most cases the data indicate a small loss ~4% in oil recovery at these higher pH's. In two cases of Intermediate and Bench No. 1 tar sands with sodium carbonate addition, processability was noticeably reduced. It is not fully understood why this occurred, but it has been predicted that the addition of carbonate to certain tar sands can increase the solubility of undesirable ions.

The effect of specific conductance and zeta potential as functions of oil recovery in separations without aeration are shown in Figures 7-22, 7-23, and 7-24. Although consistent plots of the data were obtained, these parameters are not sensitive correlating factors, with processability, as pH. Further, they are to a greater extent conditioned by the soluble and ionized salt in the water phase, that also includes at least part of the additive.

The effect of combining froths obtained from primary separation, with no air addition are discussed in Figure 7-21, with secondary recovery froths obtained by aeration of the remaining system are shown in Figure 7-25. Again the same correlation is evident, and a surprising reproducibility in the results is indicated by these combined oil recoveries in the region of 90-

96 wt% for the different Beaver River tar sands studied. Only very slightly poorer oil recoveries at pH's greater than 10, as well as less than 8, are also indicated by the data.

Sodium hydroxide give 2 to 4% lower oil loss at an equivalent pH than the other sodium salts, i.e. carbonate silicate, and tripolyphosphate, Figure 7-26. The reason for this is not evident, but a real effect appears to exist in which the anion plays some role in releasing oil suspension in the water phase. This however, does indicate that pH again in terms of hydroxyl concentration, is a main controlling factor in the chemistry of the separation.

The oil loss in the sand phase is plotted in Figure 7-27. In most cases, this is less than 1% in optimum alkaline separations. Although there is some scatter in the data, cleaner sand appears to be attained at the higher pH's of 10 to 12, rather than in the optimum region of 8 to 10 for maximum oil recovery in froth.

The solid to oil ratios obtained in the froths from primary separation with no air addition is plotted as a function of pH in Figure 7-28. Ratios from primary and secondary separation with air addition are plotted in Figure 7-29. In both these plots the scatter in the data may be resolved by drawing a line through the data on the specific types of additives used. This shows silicate and phosphate to be better additives for reducing solids in the froth than hydroxide or carbonate. However, lower amounts of solids appear to occur more in the region of 10-12 pH, than in the optimum of 8-10 pH for maximum oil recovery in froth.

It should be appreciated that the modified Pot procedure used in these studies was designed to set oil recoveries at an arbitrary level and that froth qualities do not necessarily compare. The froth qualities obtained in all these experiments are somewhat poorer. The effects indicated by the various sodium additives may be considerably reduced with proper quiescent and draining factors in larger scale separator design. Thus, lower concentrations of additives may be possible in application

Corresponding water to oil ratios in the froth as a function of pH are plotted in Figure 7-30 for primary separation. There is appreciable scatter in the data indicated by broken lines. One of the factors contributing to this scatter is presumably the manual skimming of froth employed in the laboratory operation. However, a further effect is that of the drainage rate on the froth water content.

The relationship of solids to water in terms of solid to oil and water to oil ratios is plotted in Figures 7-31 and 7-32 for primary, and primary plus secondary separations, respectively. It is interesting that a series of curves were found to occur, the parameter of which appeared to be that of the anions used in the sodium salt additives. No additive in separation also formed a further parameter. In terms of total contamination, silicate seems to be the best additive. Silicate is even better than polyphosphate, which in turn is better than carbonate, hydroxide and no additive.

The best additives may not be necessarily just sodium hydroxide or tripolyphosphate. A mixture of salts would appear to have merit. For example, silicate to minimize water-solid ratios in the froth, with tripolyphosphate to sequester polyvalent ions in solution and maximize oil recovery, blended with regular sodium hydroxide additions may be a refinement for better processability for certain types of tar sands. The concept of a mixed additive involving these and other components, such as chelating agents, is an area for further laboratory evaluation. However, in general terms this may not be necessary or is marginal for most tar sands, and a refinement applicable only to certain types of tar sands; as it has been clearly shown that in primary separation most tar sands will respond to just alkaline treatment adjusting the pH to within an optimum range of 8.5-10.5.

One of the eight tar sands designated as "Bad", which contained only 6.4% oil, compared with an average value of 10 wt% for other tar sands gave an expected poor processability (7% oil recovery) in separation with distilled water are a pH of 5.8. Further, it did not respond completely to alkaline inorganic treatment. This tar sand is understood to be a marginal surface type of tar sand, which presumably might be discarded in a commercial operation. This would solve the problem.

Figure 7-21

Chemical Adjusted Processability of Beaver River Tar Sands as a Function of Water Phase pH

(No Aeration)

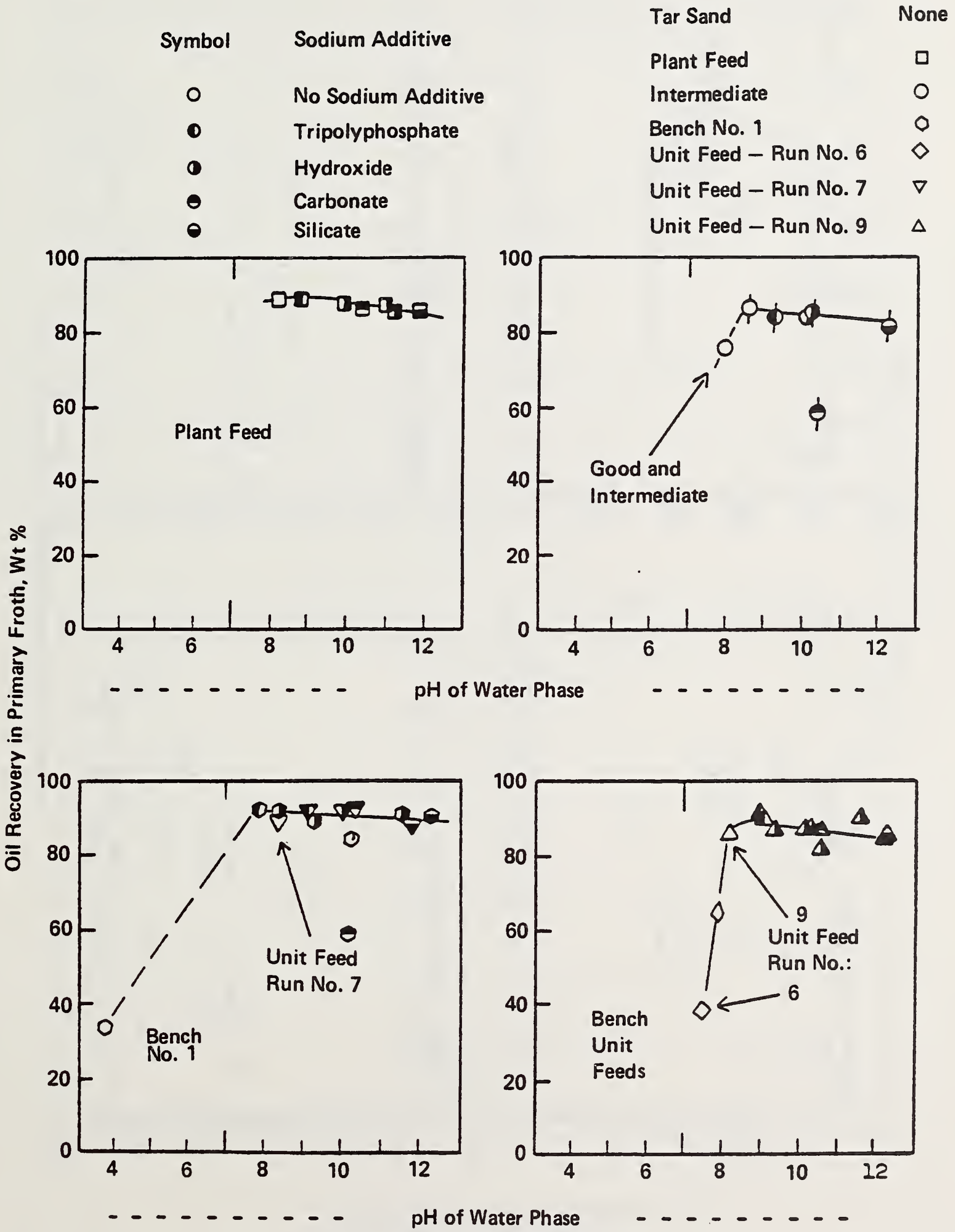


Figure 7-22

Relationship of Processability to Specific Conductance of Water Phase

(No Aeration)

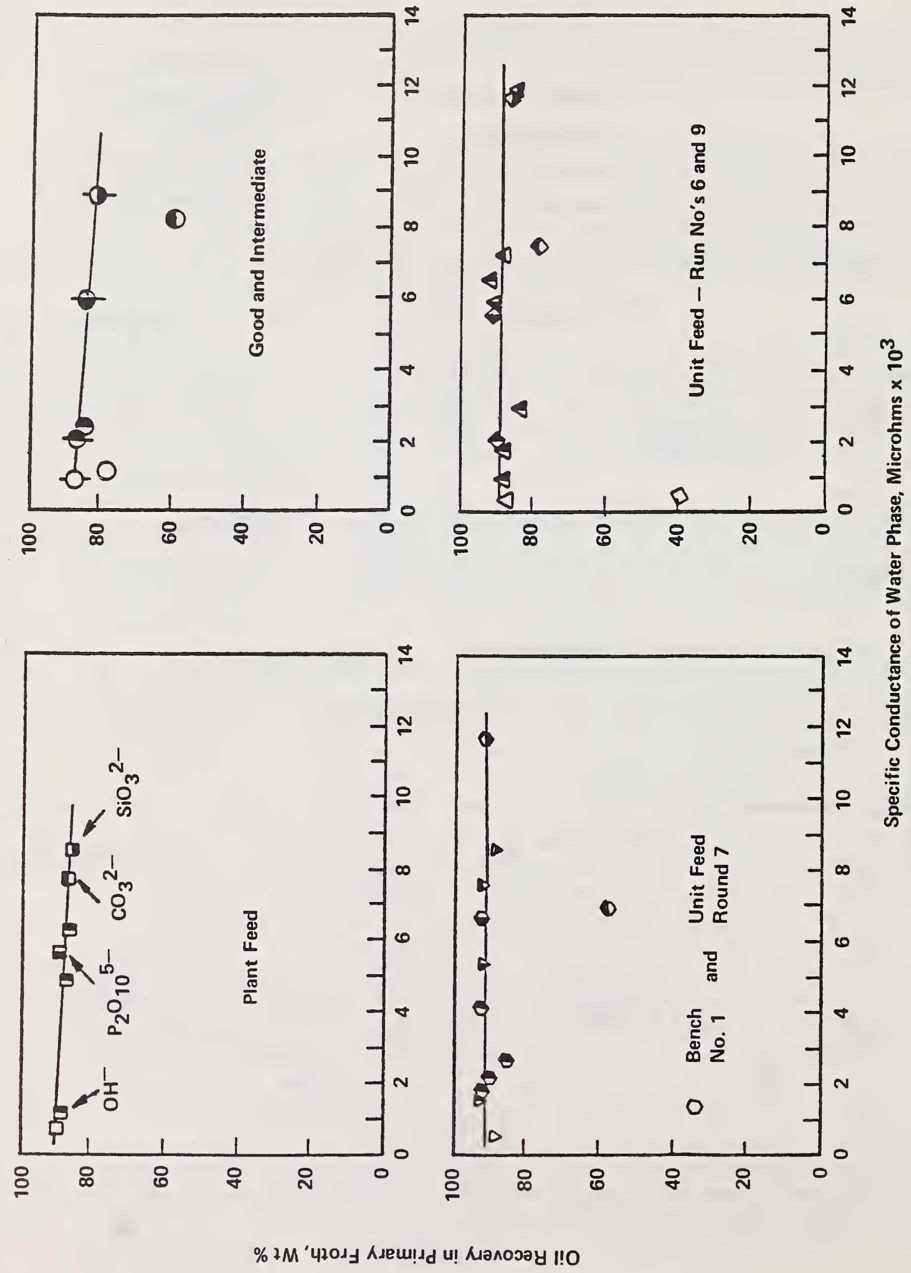


Figure 7-23

Relationship of Processability to Zeta Potential (ZP)

(No Aeration)

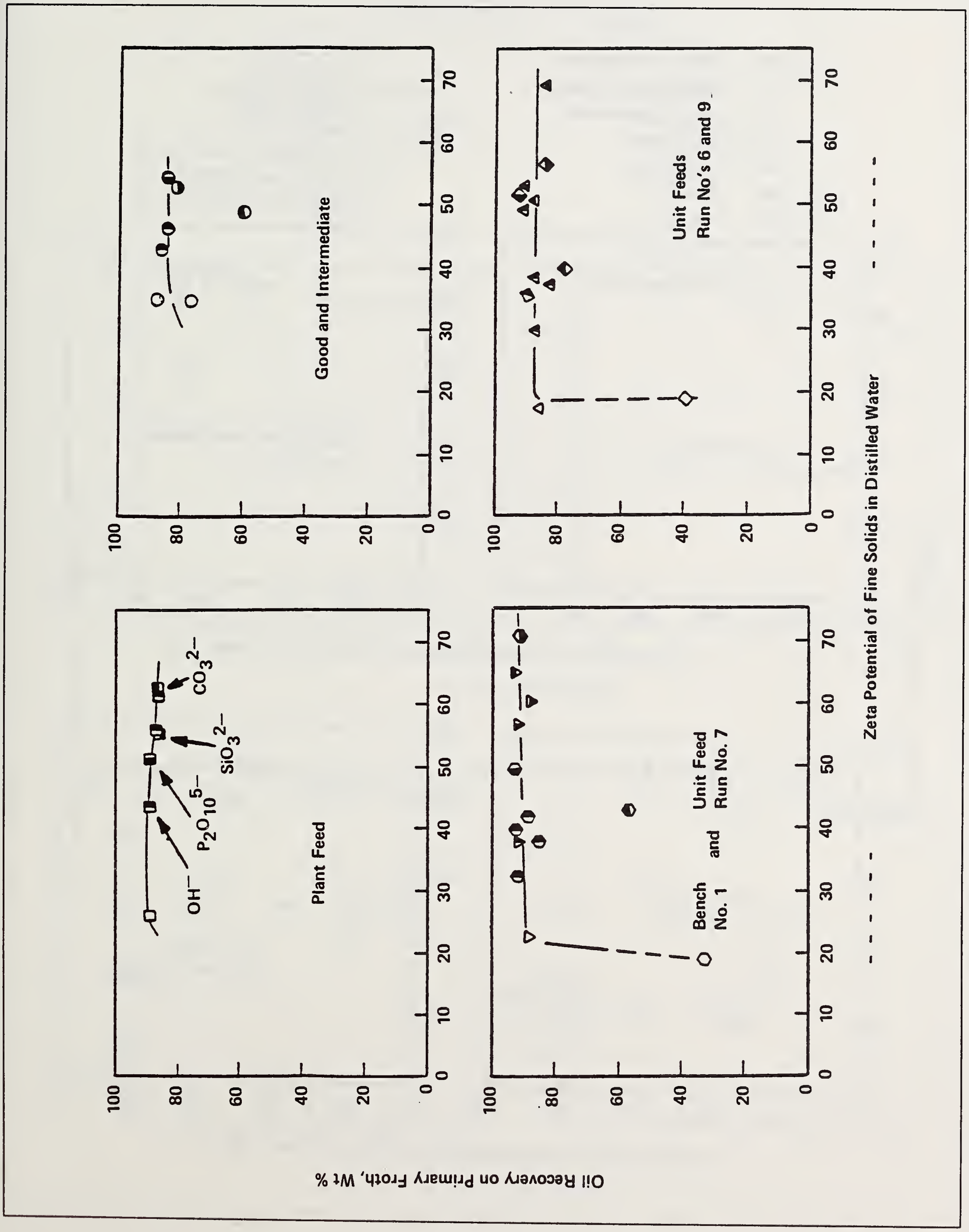


Figure 7-24

Relationship of Processability to Zeta Potential of Centrifuged Water Phase (ZP_2)

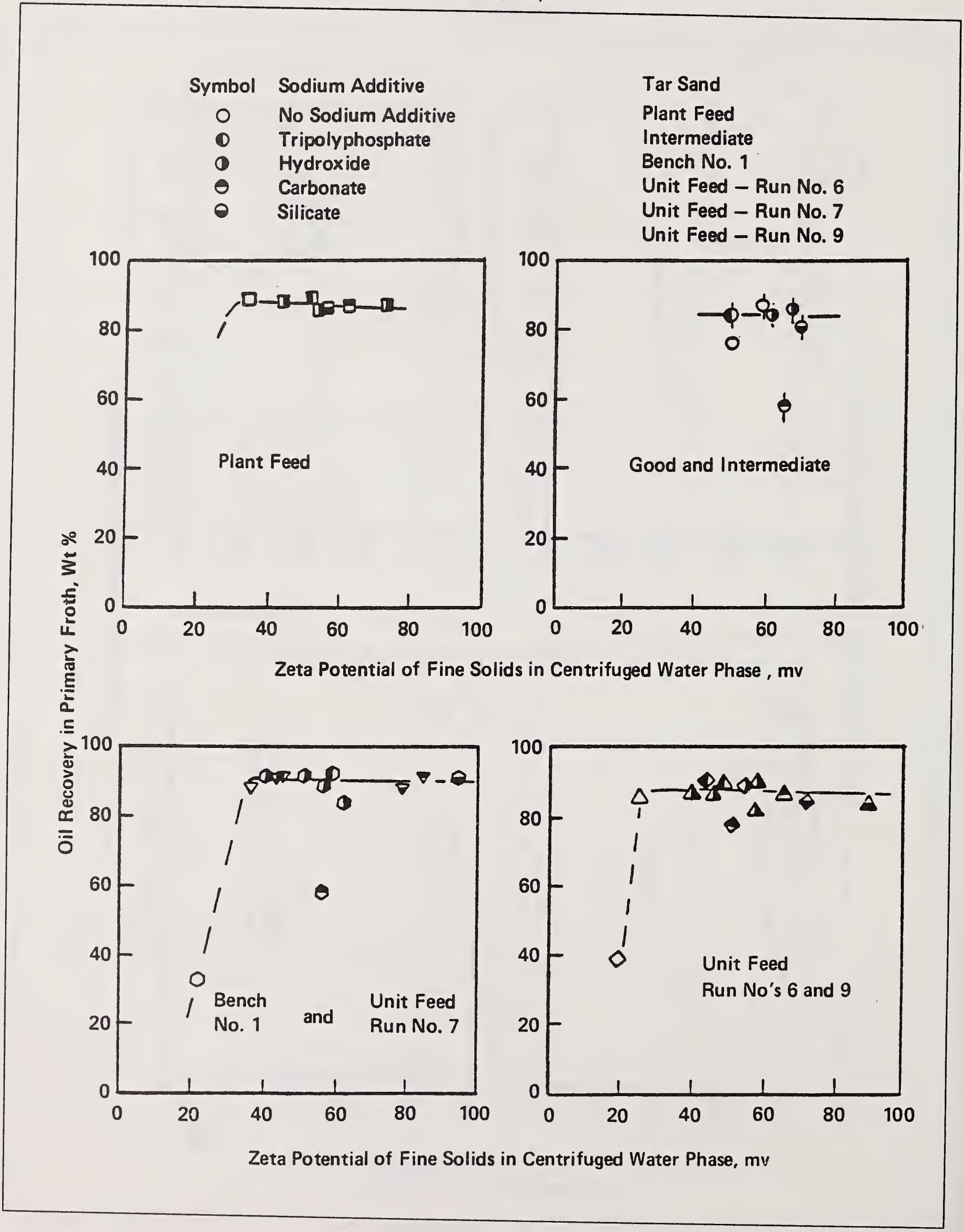


Figure 7-25

Chemical Adjusted Processability of Beaver River Tar Sands as a Function of Water Phase pH

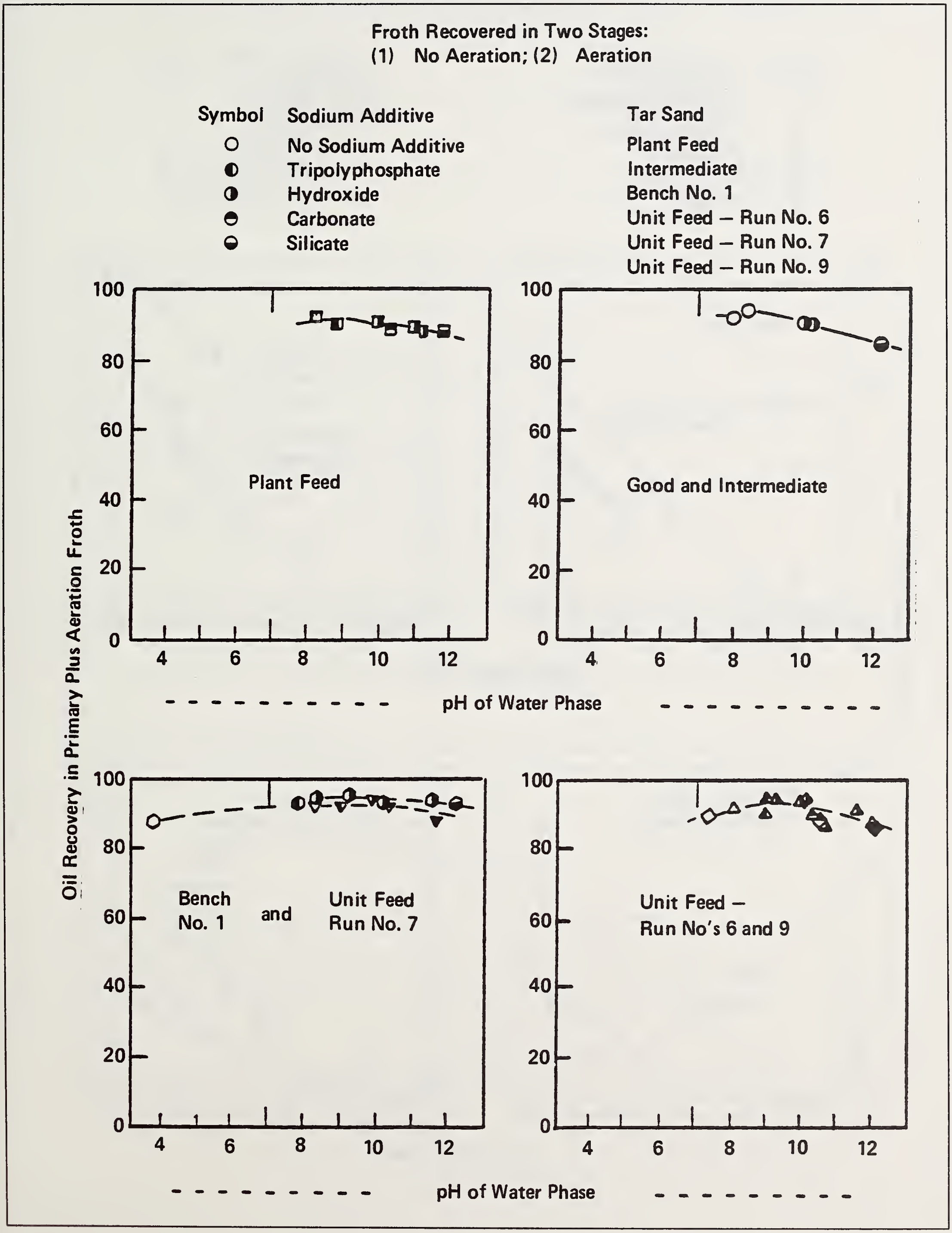


Figure 7-26

Oil Loss to Water Phase in Chemical Addition Separations as a Function of Water Phase pH

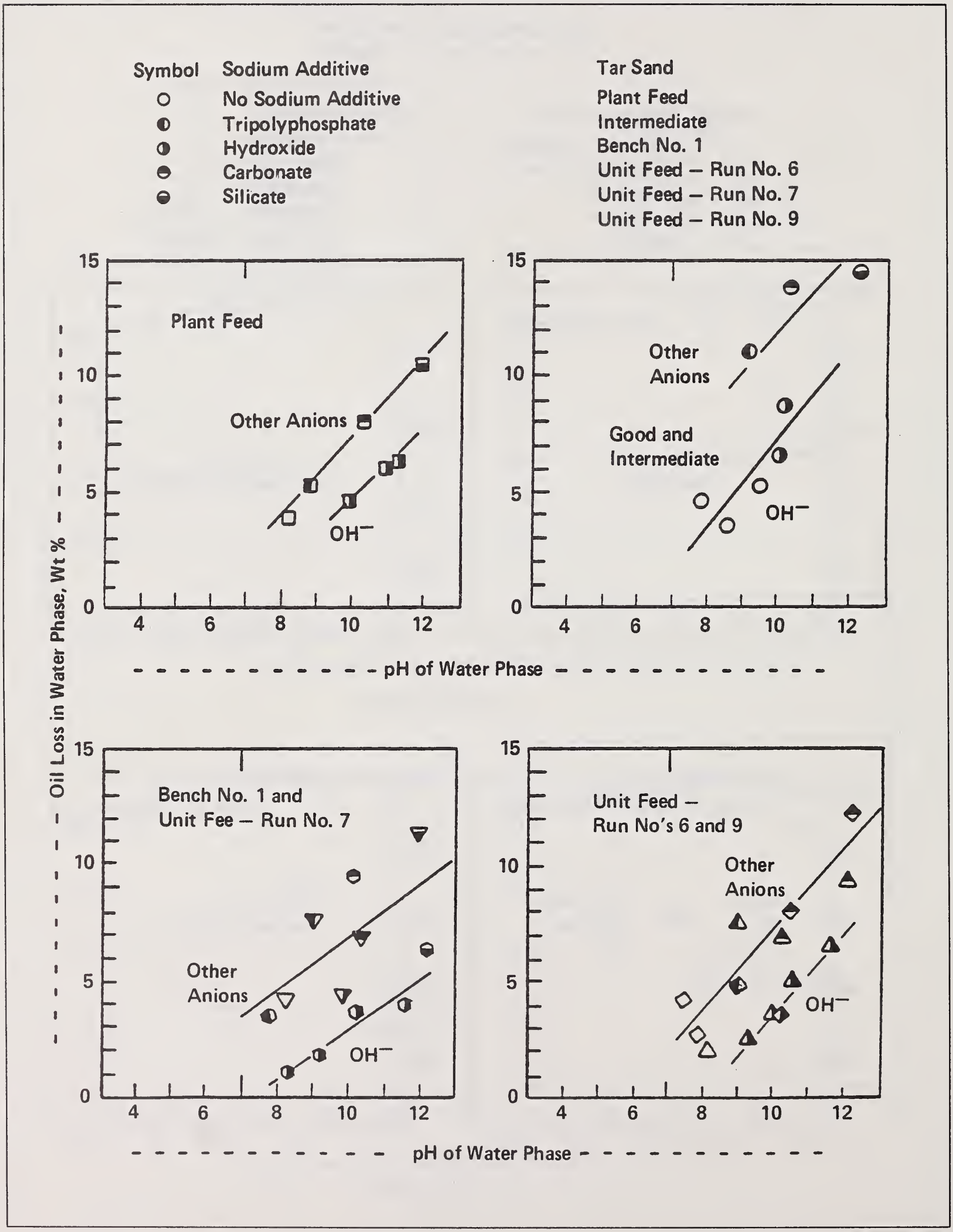


Figure 7-27

Oil Loss to Sand in Chemical Addition Separations as a Function of Water Phase pH

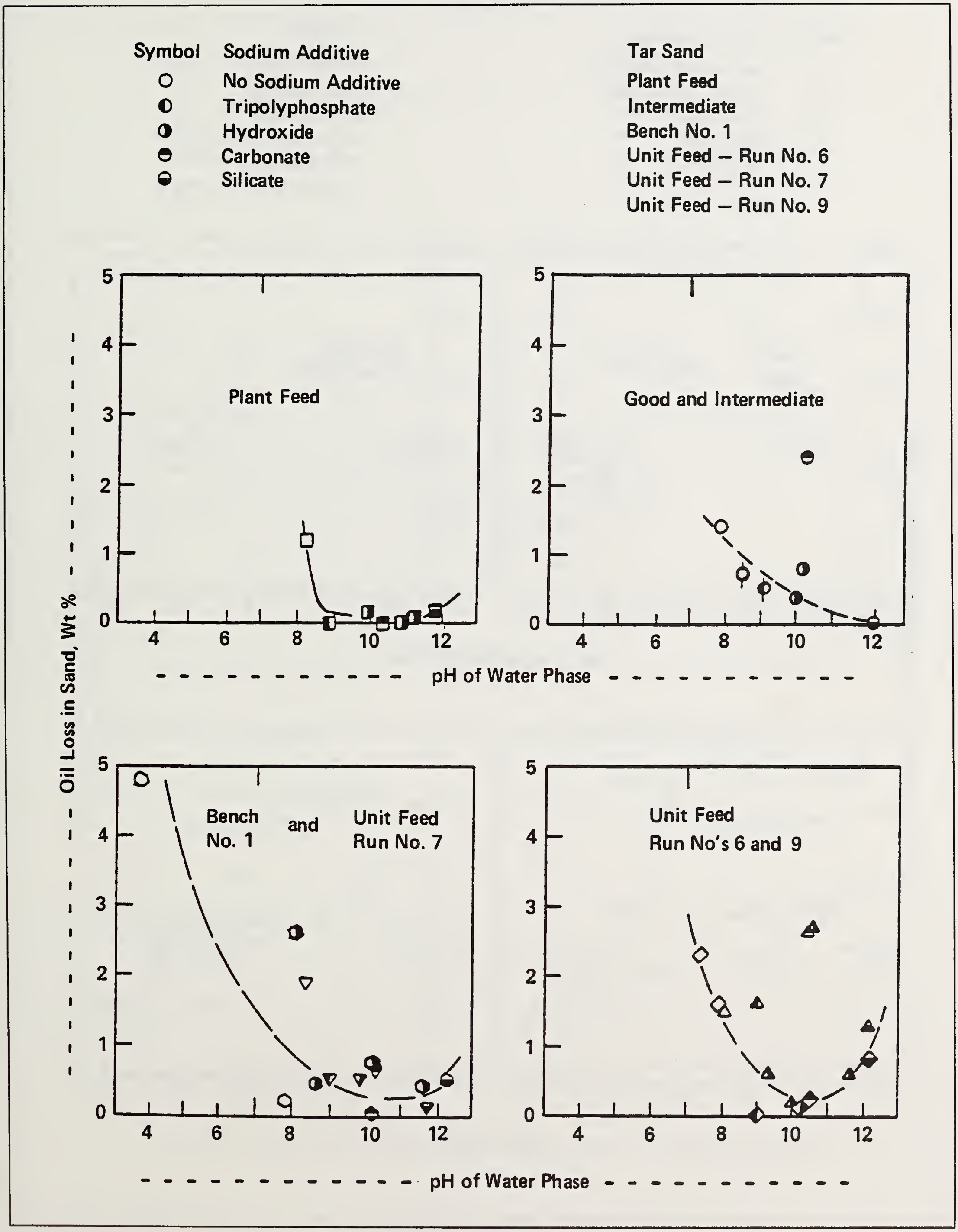


Figure 7-28

Solids-Oil in Froth with Chemical Addition as a Function of Water Phase pH

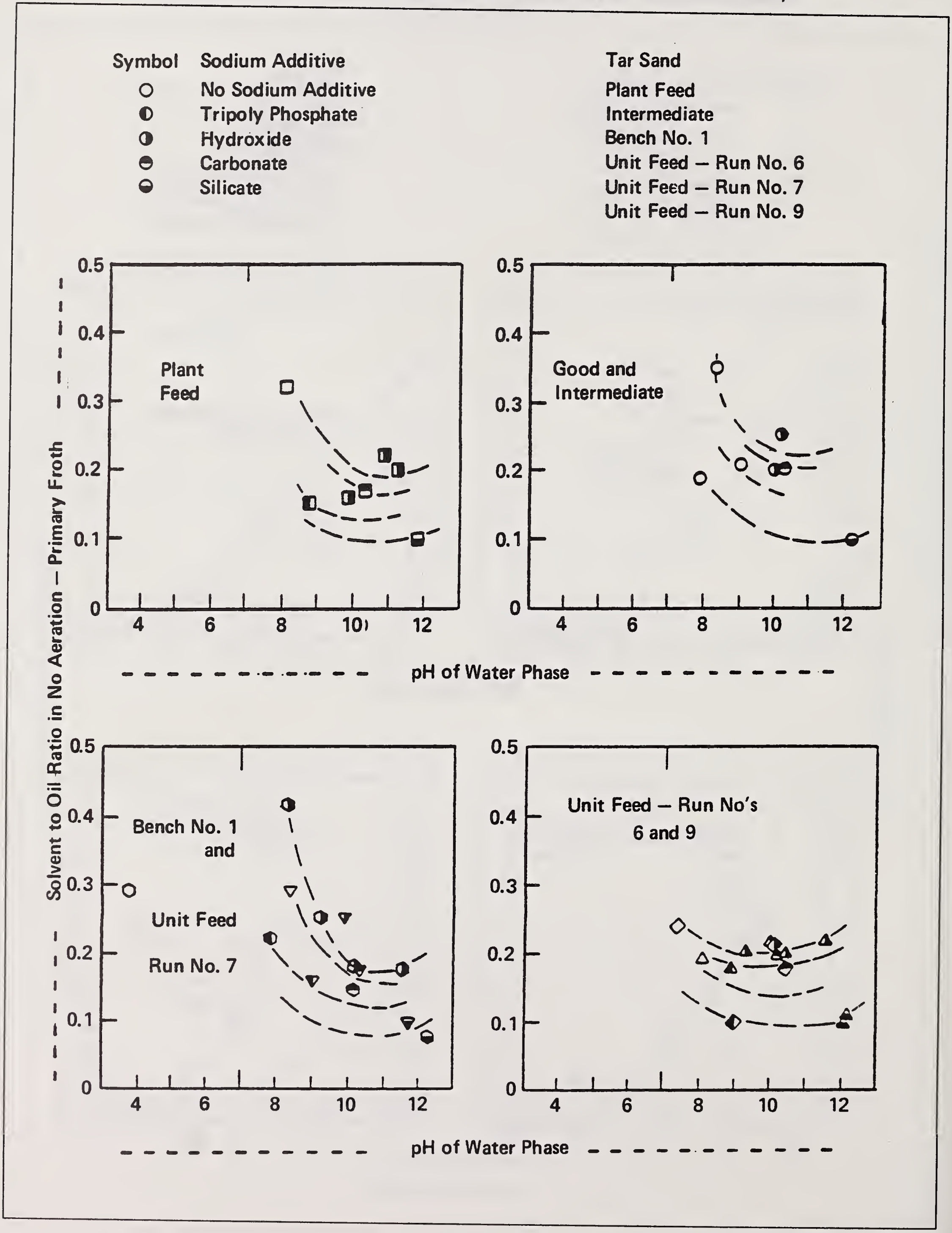
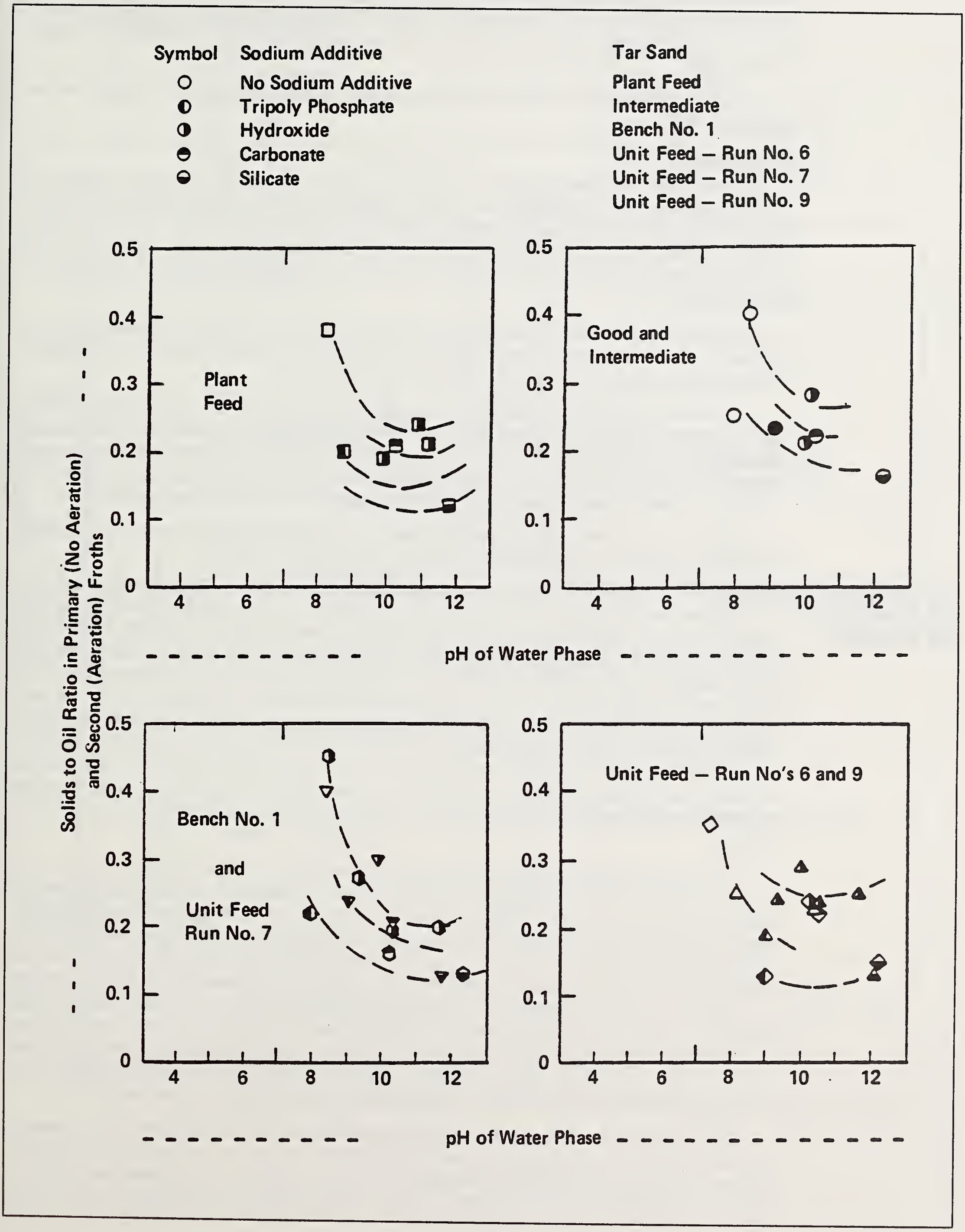


Figure 7-29

Solids-Oil Ratios in Froth from Chemical Addition as a Function of Water Phase pH



Of the additives used, tripolyphosphate was by far superior in regaining processability of this marginal tar sand. Oil recoveries of 33% in primary separation without air, and 84% oil recovery in multi-stage flotation with aeration, were attained with the lowest addition of this salt used in the study, Table 7-11. However, the available quantity of this tar sand was small, and further studies would have to be carried out on comparable new samples. The findings do indicate that with a better understanding, reasonably good oil recoveries could be obtained in a multistage process.

Upgrading marginal tar sands in flotation by chemical addition is certainly an area for continuing research.

(b) Summary

The effect of addition of simple sodium salts such as hydroxide carbonate, silicate, and tripolyphosphate on processability have been evaluated on eight different Beaver River tar sands. Most of the results indicate that an optimum processability in terms of oil recovery is achieved in the pH region of 8-10. Higher pH's of 10-12 gave good results, with only a small detrimental effect on oil recovery compared to optimum, and with perhaps some improvement in froth quality.

These studies have shown that high oil recoveries in primary separation without air may be obtained with most Beaver River type tar sands and mild alkaline chemical addition. The exception is marginal surface tar sands with low oil - higher clay content.

The anion of the sodium additive is not as important as the resulting pH condition in terms of oil recovery, but has a significant effect on froth quality. Primary separation without aeration does not appear to appreciate the anion of the additive as much as has been observed in previous studies with aeration. In these studies silicate and tripolyphosphate were the best additives. Although, this tends to confirm previous findings with aeration, the effect is less dramatic.

Specific conductance and zeta potential both are less sensitive parameters of processability than pH, and appear to be related only in extreme and limiting conditions.

7-9 Pre-Washing Studies

Because large amounts of chemicals were required in the phosphates addition studies discussed above, and appreciable amounts of soluble salts were found to be present in these particular tar sands, pre-washing of tar sands was evaluated to remove the soluble salts followed by pH adjustment. A few exploratory studies were therefore carried out and the results are discussed in this section. The experiments were planned to compare a standard separation in the pot with separations carried out on tar sands washed with either water or sodium salt solutions, such as tripolyphosphate, silicate, and hydroxide. The procedure was to slurry as in the pot procedure, screen (325 mesh) the slurry and centrifuge out solid material. The recombined wet solids and oil slurry was washed again, for a total of three washings. The washed tar sands was then separated using the standard procedure, while the washings were analyzed for salt content and ion type.

The particular sample of tar sand feed used in this study, exhibited an even poorer processability than that used in the phosphate study. Separation conditions were maintained the same in all experiments except for the different solutions used and pre-washing. The first eight experiments of this series of twelve all processed poorly, which appears to reflect the low pH, which in all cases was about 3 or less. The low oil recovery and high solids in the froth could be attributed to the acid conditions. However when a low concentration of sodium tripolyphosphate was used a remarkably good separation was achieved. Sodium silicate and to a lesser extent sodium hydroxide at very low concentrations gave values intermediate between the blank and the good result with sodium tripolyphosphate. Sodium silicate was at an equivalent pH, however sodium hydroxide was at a high pH of about 12 which would also contribute to poor processability. Further, poor processability was obtained at high sodium tripolyphosphate concentrations.

These experiments with sodium tripolyphosphate do tend to substantiate the earlier proposal by Karl Clark of pre-washing as a method to improve separation. Although the same total amount of chemical used in separation could achieve the majority of the improvement, Table 7-12. The threshold level of soluble salts in the tar sands at which pre-washing may give an im-

Figure 7-30

Water-Oil Ratios in Froth from Chemical Addition Separations as a Function of Water Phase pH

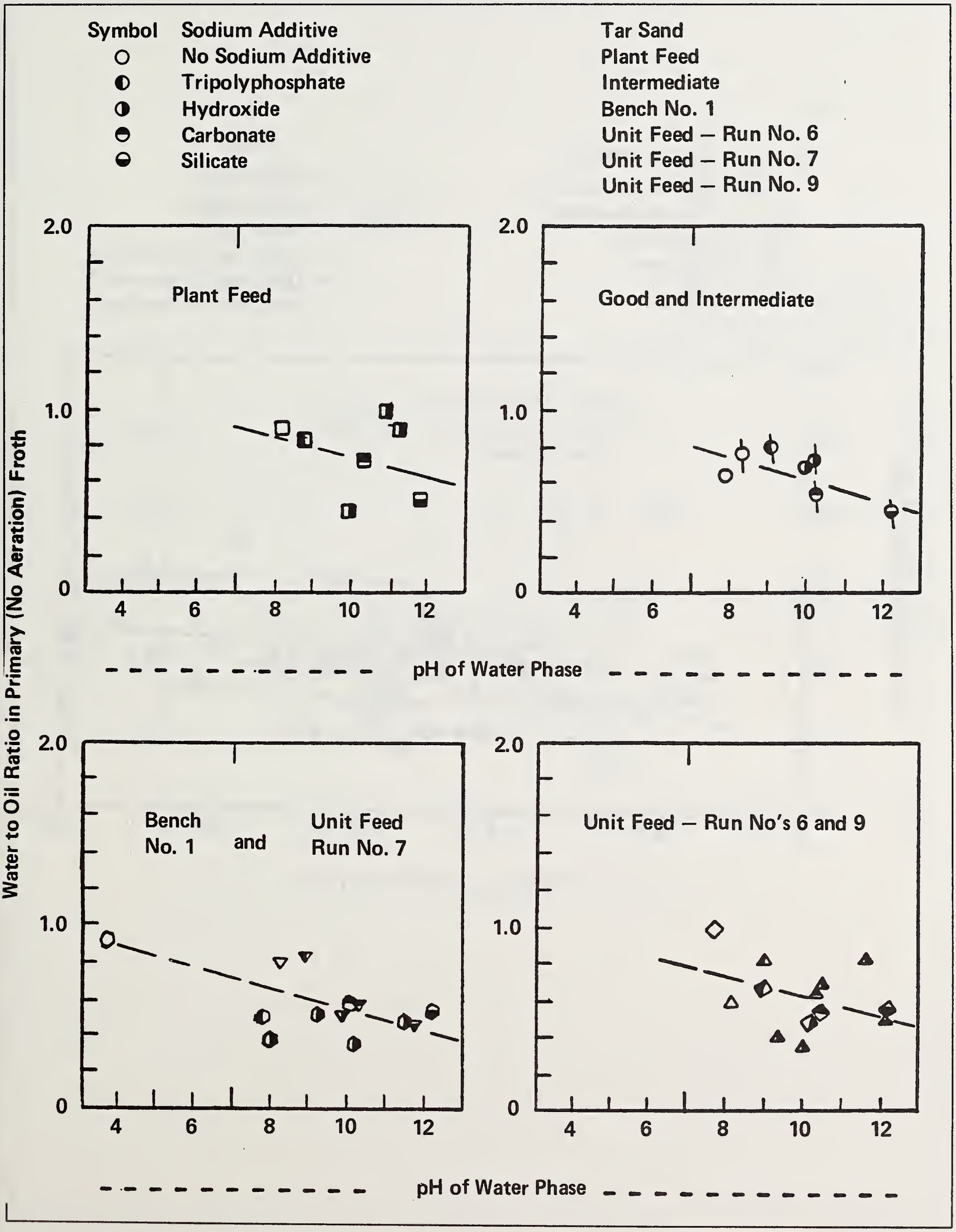


Figure 7-31

Relationship of S/O and W/O Ratios in Froth with Chemical Addition to Different Beaver River Tar Sands

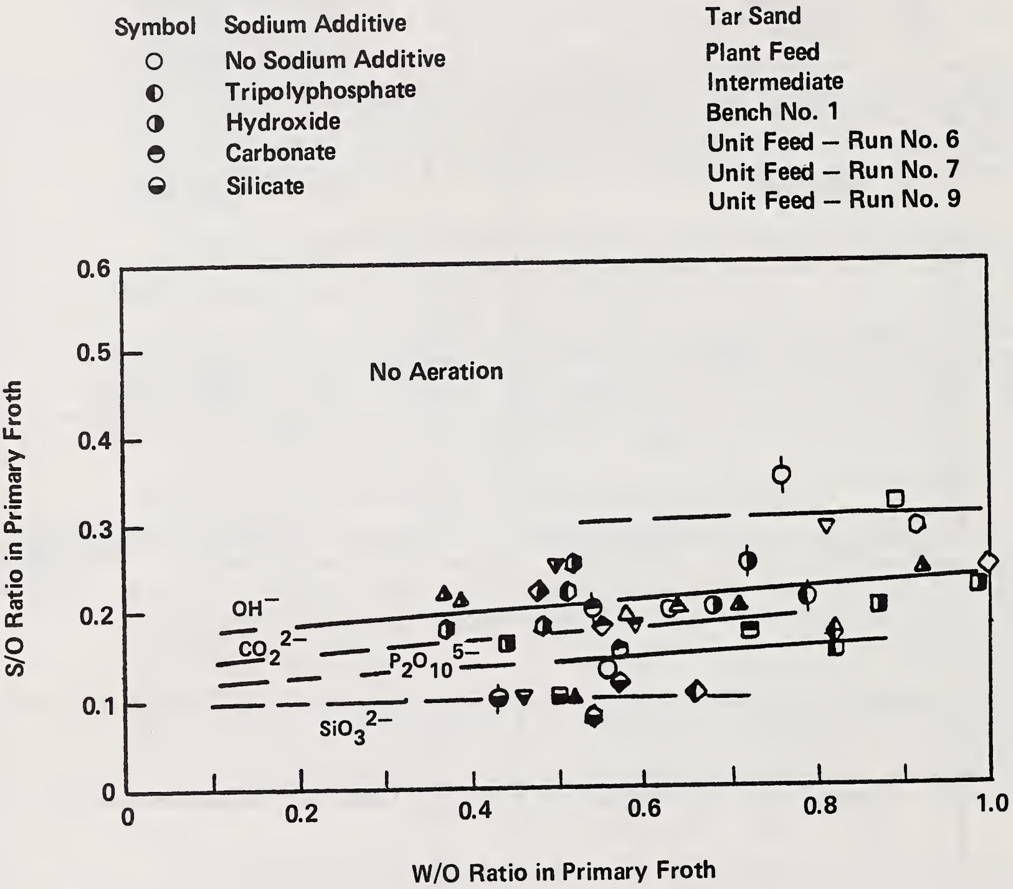


Figure 7-32

Relationship of S/O and W/O Ratios in Froth with Chemical Addition to Different Beaver River Tar Sands

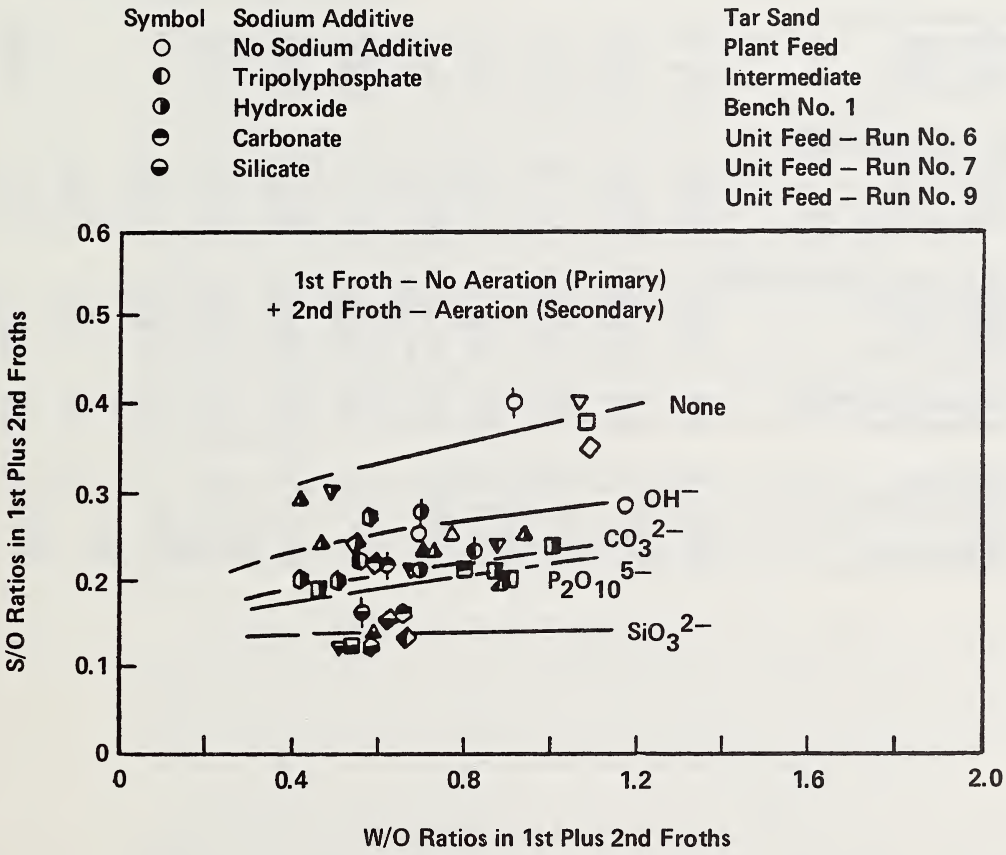


Table 7-11

Chemical Adjusted Processability of Beaver River Tar Sands

Tar Sand (Designation)	**Bad**										
Sodium Additive (In Mixing)	**None**	**Hydroxide**				**Tripolyphosphate**				**Carbonate**	**Silicate**
Amount of Salt, Wt % On T.S.	0	0.06	0.12	0.24	0.40	0.30	0.40	0.80	2.40	0.57	0.66
Amount of Sodium, Wt % On T.S.	0	0.04	0.07	0.13	0.23	0.09	0.12	0.24	0.72	0.24	0.24
No Aeration Froth											
Solids/Oil Ratio	3.08	0.66	0.36	0.29	0.41	0.22	0.23	0.31	--	--	0.93
Water/Oil Ratio	4.44	2.29	0.94	0.87	0.69	0.66	0.94	1.15	--	--	1.38
Oil Recovery, Wt %	7.0	5.5	18.5	16.5	14.0	33.3	28.4	16.3	0	0	4.6
No + 1st Aeration Froths											
Solids/Oil Ratio	5.41	0.55	0.50	0.29	0.36	0.44	0.31	0.41	1.06	0.53	1.07
Water/Oil Ratio	9.40	1.43	1.37	0.70	0.92	1.07	1.06	1.40	2.29	1.65	1.29
Oil Recovery, Wt %	30.6	62.7	73.7	76.4	58.5	80.8	68.0	74.2	7.5	30.5	13.4
No + 1st and 2nd Aeration Froths											
Solids/Oil Ratio	5.79	0.66	0.51	0.35	0.33	0.67	0.46	0.49	0.98	0.61	1.72
Water/Oil Ratio	9.95	1.97	1.22	0.88	1.03	1.65	1.48	1.43	2.45	1.61	1.65
Oil Recovery, Wt %	51.4	74.0	80.3	78.6	61.9	84.4	79.5	81.6	22.5	41.3	15.6
Oil Loss In Water Phase	26.5	19.7	19.2	19.8	37.6	13.7	17.5	13.5	71.7	57.8	83.0
Oil Loss In Sand	22.1	6.3	0.5	1.6	0.5	1.9	3.0	4.9	5.8	0.9	1.4
Water Phase	5.9	7.7	9.3	9.6	11.3	7.1	7.1	7.9	8.7	10.2	11.4
Zeta Potential, ZP$_1$	21	36	34	49	42	47	41	54	52	40	49
ZP$_2$	25	44	46	(65)	(55)	43	53	(72)	(69)	(51)	(65)
Conductance, C$_2$	782	1496	1768	2652	5372	2720	3128	5644	13,600	6800	8840

provement and chemical addition advantage is unknown. Considerably more work would have to be done in this area, if merited. There is however a disadvantage to this approach in the costly and large equipment required to effect pre-washing presumably in a counter-current process system.

However from a point of view of understanding the process, it is interesting that washing of soluble salts from the tar sands and conditioning with sodium tripolyphosphate achieved good results in subsequent separation in water. This is consistent with previous general findings on sodium tripolyphosphate. It might also be noted that in the three experiments in which sodium tripolyphosphate was used, the highest zeta potential values of suspended particles in the water phase were obtained. This again indicates that sodium tripolyphosphate is a most effective dispersing agent for the system.

(a) Water Soluble Salts

As water is the separating medium of solids and oil, both in the tar sand structure and in processing, then all the physico-chemical properties of the surfaces will be related to the separating water phase. The amount of ions in solution will therefore have a profound effect on the system. Water washing studies like those discussed in the previous section were carried out on different tar sands. Acid and sodium salts of weak acid solution washing was also performed. Within experimental error, the same amount of salts were removed regardless of the washing media. Emission spectrographic analyses were carried out on the salt after evaporation of the washings. The salts were indicated to contain majors of calcium with magnesium, iron, manganese and alumina by emission spectrograph analysis. Ethylenediaminetetraacetate (EDTA) titrations on washings confirmed these analyses, giving values of about 10% calcium, 5% magnesium and 15% iron on total salts. The different washing solutions, i.e. water, sodium hydroxide, silicate, phosphates, etc. all gave about the same amount of calcium and magnesium in the salt, as measured by EDTA titrations. It was tentatively concluded that in the period of washing, very little additional ions went into solution from the parent minerals or were desorbed from clay minerals.

The results of water washing of "aged" Hole 11 and "fresh" Beaver Creek tar sands were shown in Table 4-38. The soluble salts in Beaver Creek tar sands were 0.058 wt% which is less than one tenth of that in the aged Hole 11. The value for Beaver Creek tar sands is of the same order of magnitude found by Clark in his earlier studies, i.e. 0.05, 0.04 and 0.02 wt%, see Section 4-1-2.

The two sets of data in Table 4-38 illustrate the reasons for poor processability. An interesting observation is that the sodium content is higher in the Beaver Creek salt, whereas it is only a large trace in Hole 11. This is directionally the effect of the Ca/Na ratio on flotation of silica, which was discussed in Section IV, but not of exactly the same order of magnitude. The sodium content of the soluble salts from Hole 11 is a minor, presumably by virtue of the large amount of Ca, Fe, Mg, Mn, and Al which has gone into solution from oxidation and generated acidity.

As calcium is a major and magnesium behaves similarly in solution, the criteria of free calcium at equivalent concentration (taken from the literature) are shown in Figure 7-33 plotted against the oil recovery in froth from separations at equivalent concentrations with the different phosphates. Equivalent concentrations in this plot are only relative, and the relationship shown is only to point out that theoretical arguments are fairly consistent with observations and data on hot water extractability effects.

(b) Oil Soluble Component

It was interesting for example that the salt extracted from the aged Hole 11 tar sands (Table 4-30) also contained a quantity (0.2%) on tar sand of water soluble organic material. Presumably this is either a component of the oil or a product of oil oxidation. This water soluble component was analyzed and found to contain 42% C, 7% H, 12.5% S and 0.1% N. By difference, oxygen would be extremely high, if other elements were not present. The structure appears aromatic from IR and MNR analyses, although a calculated formula would suggest a naphthene from the elemental analysis. Although these results are questionable due to the very small sample available for analysis, they are interesting and worthwhile recording. It would appear

Table 7-12

Effect of Prewashing Tar Sands

Prewashing Solution	--- None ---		Sodium Tripolyphosphate
Concentration, Wt% Sol^n	------------		1.0
Salt Amount, Wt% on Tar Sand	------------		2.4
Separating Solution	Water	NaTPP	Water
Concentration, Wt% Sol^n	-	8.0	-
Salt Amount, Wt% on Tar Sand	-	2.4	-
Froth Composition, Wt%			
Water	42	29	44(1)
Solids	40	24	15
Oil	18	47	41
Solids-Oil Ratio	22	0.5	0.36
Oil Recovery in Froth, Wt%	42	87	91
Separated Water Phase			
pH	2.7	7.8	8.9
Zeta Potential	11.5	32.5	38.0

(1) This value may be high due to emulsification of water in prewashing.

Table 7-13

Effect of Soaking on Separation

Sodium Tripolyphosphate	----- No -----		----- Yes -----	
Soaking for 1 hour at 180°F	No	Yes	No	Yes
Froth Composition, Wt%				
Water	42	29	29	32
Solids	40	52	24	21
Oil	18	19	47	47
Solids to Oil Ratio	2.2	2.7	0.5	0.45
Oil Recovery, Wt%	42	51	87	86
pH of Separated Water Phase	2.7	3.3	7.8	7.6

from the analysis and water solubility that this material is perhaps an organic sulphate and certainly not a basic nitrogen compound.

(a) Soaking

The basic idea was to explore very briefly any rewetting in the process that might not be completed in mixing. This was attempted by using a soaking time of one hour at 180°F after mixing and before flooding in the standard Pot separation. The results are shown in Table 7-13. In the base case that was acid, no change in froth quality was found, but 9 wt% lower oil recovery resulted with soaking. This was presumably due to some interfacial change reducing oil-gas attachment. A second comparison was made with the addition of sodium tripolyphosphate. In this case separations were essentially equivalent.

These results show no advantage for further solution contact (soaking) after the standard mixing time employed in the Pot procedure. This supports the view that the hot water separation process is a physical method of separating the tar sands. The degree of separation is dependent on the tar sand state, and a chemical balance is required to modify the interfaces in order to obtain improved processability.

7-10 Basis For Chemical Addition

In a commercial operation high recoveries and good quality oil must be maintained in spite of variations in tar sand quality being fed to the process. A constant yield and quality of separated oil may be possible by continuous adjustment with chemical addition in one or more stages of the process sequence. It is, therefore, of prime importance to know how adjustment must be made to allow for changes in feed quality. It should be noted that even <1% improvement in oil recovery may be worthwhile for capital investment.

No chemical addition is needed for good quality naturally alkaline oil sands that separate readily with high oil recoveries and low water-sand contaminated froths, other than minor additions of caustics.

When acidity has been generated by oxidation in either exposing, working and storage or by natural processes in the formation, small amounts of chemicals, e.g. NaOH,Na_2CO_3 etc. will be required to adjust this tar sand acidity to a slightly alkaline pH of 9 ± 1 to recover good processability. The buffer action of the clay appears to be a main problem, in that these added salts are adsorbed. Thus, pH control should be used only in specific instances for good economy. Methods of overcoming the buffer action, such as salt (NaCl) addition together with a pH controller may be useful in some cases. Although, some neutral to acidic tar sands can be corrected with just sodium hydroxide addition. pH is obviously not the only factor.

Poor quality tar sands located particularly in the upper part of the formation, require more than just pH control. Specific additives such as sodium polyphosphates are necessary to restore processability by sequestering divalent ions, i.e. Ca/Hg. Hence, chemical mixtures balanced to precipitate and complex deleterious cations present, and to maximize the surface charge under "buffered" pH conditions of 9 ± 1, may provide maximum improvement. However, the maximum yield of 80-85% obtained with both low oil Area D tar sands (Hole 11 and Hole 21A) suggest that there is another factor involved in poor processability. This appears to be more of a permanent loss of oil through attachment of the solids to oil. If this is the result of water loss from the structure, then work would have to be done to rewet the solid with water. Longer mixing times may be helpful in alkaline media, although combined chemical and mechanical work can also contribute to flocculation of clay. This aspect requires further study.

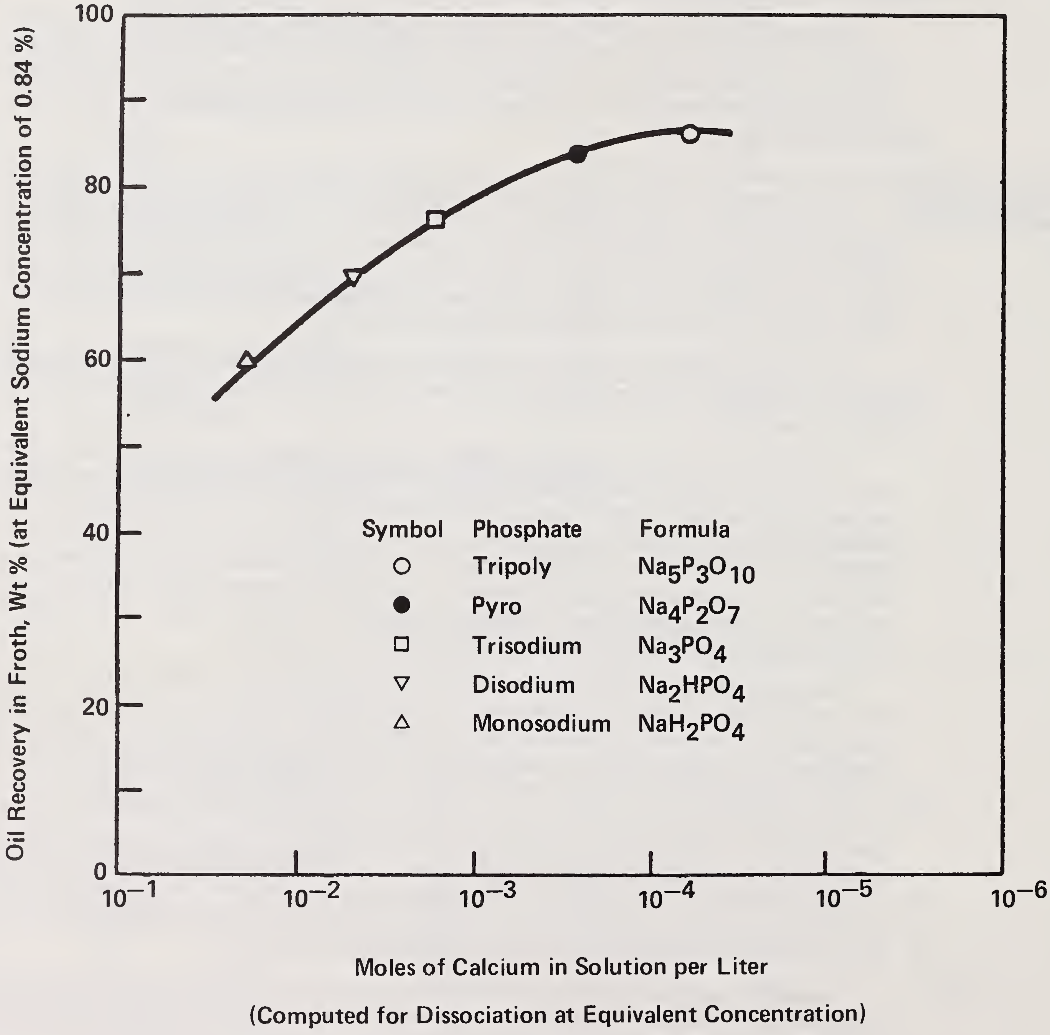
Hence, the application of chemical addition in control of the process for an economic oil production will necessitate continuous key measurements of the system to be made, which have been firmly correlated with processability. Besides clay-oil contents and pH, other measurements may be needed, i.e. zeta potential, Ca/Hg ionic strength, etc.

C. Organic Additives

As naturally occurring surfactants have been found to be an important factor in the Hot Water Flotation Process, it is logical to evaluate the addition of other organic compounds from

Figure 7-33

Relationship between Oil Recovery with Phosphate Addition and Free Calcium Ions at Equivalent Concentration



the many that are available commercially, for effects and enhancements. Further, as polyvalent ions are bridging agents in solids/bitumen association, organic compounds that complex or sequester these ions were preferentially selected in these preliminary studies.

7-11 Sodium Oxalate

An homogenized, acidic, Hole 11 tar sand that had been in storage for about a year was used in the oxalate study. The feed contained 7% oil, 10% water and 12% fines. This poor quality tar sand was selected so that large improvements in separation could be readily measured in order to differentiate between the effects of pH and those of the oxalate ion.

Separations were carried out using the standard Pot procedure, except that ash analyses were used to determine oil associated with solids in the water phase and the sand. This approach is adequate for exploratory studies of this nature, and saves time. Chemical additions were made in mixing only, and distilled water was used in flooding. Sodium hydroxide solutions were made up fresh just prior to separation.

The oil recovery results from the two series of experiments with and without the addition of a constant amount of oxalic acid, and in which sodium hydroxide was also added to change the pH, are shown in Figure 7-34. The beneficial effect of oxalate on separation is shown quite clearly by the data. However, only a small improvement in overall oil recovery was realized with increasing pH.

The oxalate effect on froth quality is shown in Figure 7-35. The lower water and higher oil content represents a significant improvement. The solid to oil ratio was also significantly reduced in separations with oxalic acid addition. Details of the experimental results are summarized in the Appendix.

This study was conducted at a constant low oxalic acid addition, while varying the pH by sodium hydroxide addition. The next logical step was to vary the oxalic acid addition. This was done at a constant sodium hydroxide addition. The results are shown in Figure 7-36.

It was found that as the oil recovery increased, the solids to oil ratio decreased only very slightly, and the froth quality improved with increased oxalic acid addition. However, the higher the oxalic acid concentration the lower the pH and the better the separation, which is unexpected unless the oxalate anion is strongly reacting in the system. This suggests that for higher oil recoveries larger quantities of oxalic acid were required at the optimum pH of 9 ± 1 than was needed in the first series of experiments.

Other experiments with higher oxalic acid addition (0.5 wt% on tar sand) were unfortunately over compensated with sodium hydroxide giving a high final pH of about 12 . This resulted in lower yields as would be expected . It should be noted however, that the solids to oil ratio attained in these experiments were lower than in all other experiments with oxalic acid addition.

Oxalate can react as a reducing agent, but can also react with polyvalent ions, i.e. precipitation. The role of the oxalate as either a reducing agent or a precipitating agent or both has not been made clear by this study. However, an improvement attributable to the oxalate anion has

Figure 7-34

Effect of Oxalate and pH on Oil Recovery

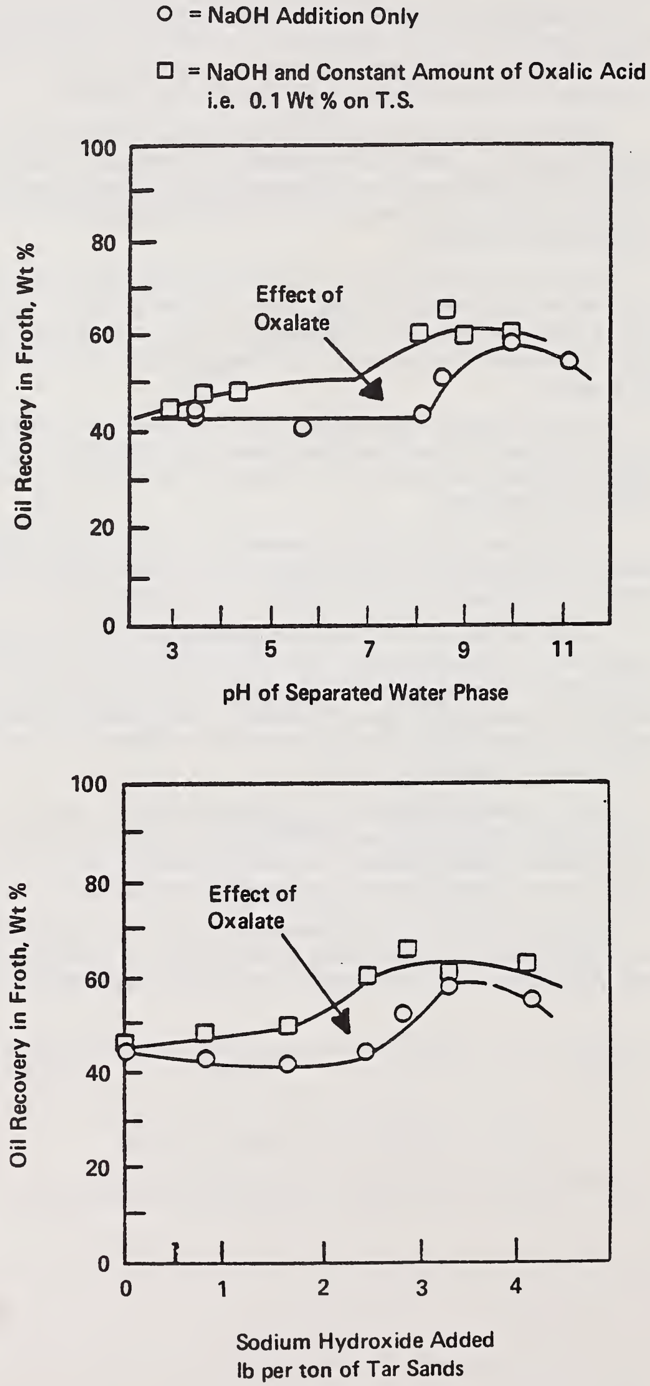


Figure 7-35

Effect of Oxalate and pH on Froth Composition

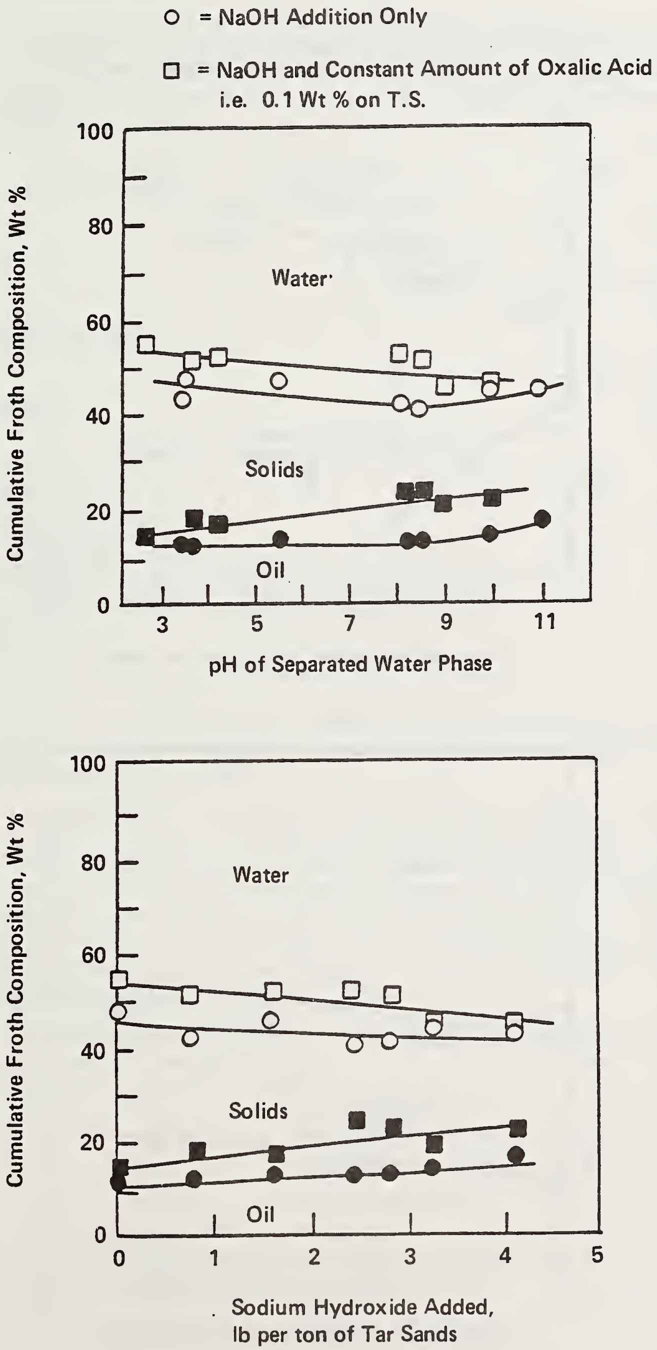
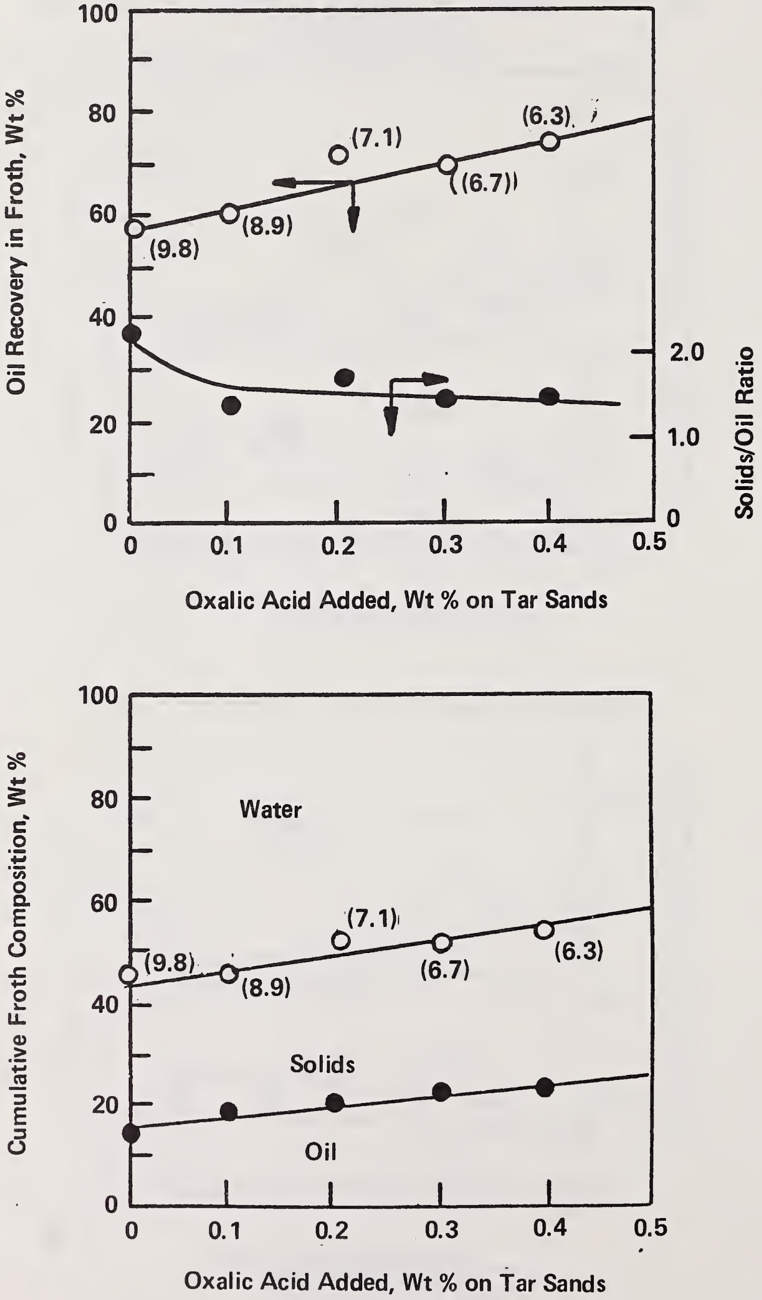


Figure 7-36

Effect of Oxalic Acid Addition at Constant Sodium Hydroxide Content (pH of Water Phase is Shown in Parenthesis)



been confirmed. Very significant improvements realized by sodium oxalate in separation of poor quality tar sand is only obtained with appreciable quantities of additive e.g. 2lb/tonne of tar sands The cost is probably be prohibitive, but the effect should be evaluated further as a diagnostic tool on mechanisms.

7-12 Pyridine

The addition of pyridine in separation was tried on the basis that it is a very powerful solvent for removing residual hydrocarbons adsorbed on the solids. The mechanism proposed was that pyridine complexed with active solid sites displacing hydrocarbons. A separation comparison showed:

Table 7-14

Effect of Pyridine Addition

	Blank	Pyridine*
Froth Composition, Wt%		
Water	45	54
Solids	19	15
Oil	36	31
Solids/Oil Ratio	0.53	0.48
Oil Recovery in Froth, Wt%	82	84
Oil Loss in Sand, Wt%	8	3
pH of Water Phase	6.3	7.2

* 0.1 Wt% on Tar Sand

It can be seen that there is essentially no significant difference at the concentration level of pyridine used. Directionally there appears a very slight tendency of pyridine addition to reduce the oil associated with solids.

7-13 Surfactants

There are thousands of surfactants available on the market. The dilemma is where to start in the evaluation of the effect of surfactants in the hot water flotation process. The approach taken in the present study was to investigate the effects of (a) type, (b) hydrophilic-lypophilic balance, and (c) molecular weight of a particular class. The concentration of the surfactant has been kept fairly constant in these preliminary evaluations. Thus, the separations discussed in this section are exploratory and were carried out mainly to observe any effects resulting from the addition of organic surfactants.

Surfactants readily available off the chemical shelf were used in these preliminary studies. These may be summarized as follows:

	Type	Chemical Chosen
1.	Nonionic	Polyoxyethylene in polypropylene base, and pine oil
2.	Anioni	Versene and cresylic acid
3.	Cationic	Ethylene diamine and hyamine
4.	Amphoteric	Alanine
5.	Polymeric	Sodium carboxy methyl cellulose
6.	Fluorocompounds	perfluoro hexane
7.	Silicone	antifoam "A" silicone

A Hole 11 tar sand was used that was adjusted to slightly basic condition by the addition of a mixture of sodium hydroxide and sodium tripolyphate. This was used to give a minimum basic condition for good separation and still provide latitude for any beneficial effects of surfactants to show up in the froth.

The results of addition of these surfactants are shown in Table 7-15. It can be seen that on the basis of oil recovery classes 5 and 6 gave poorer results. A small improvement with ethylene diamine (class 3) is attributed to a more favourable pH condition.

Classes 1 (nonionics), 2 (anionics) and 4 (amphoterics) gave significantly improved separations. Other studies, see Appendix, are not always positive. For example, Versene, known to complex and remove undesirable calcium, gave poorer results with a very low oil tar sand from Hole 21A that was high in fines. Poorer results were also obtained with an antifoam amino-sulphonate (amphoteric).

7-14 Hydrophile-Lypophile Balance (HLB)

The HLB of a surfactant or mixture of surfactants is an expression of the balance of the size and strength of the hydrophilic (water-loving) or polar and the lypophilic (oil-loving) or non-polar groups. An HLB scale of 0-20 is used in which the lower half refers to lipophilic type surfactants and the upper half refers to hydrophilic type surfactants. HLB and solubility are related in that low HLB will tend to be oil soluble and high HLB will tend to be water soluble. Although there are exceptions, surfactants in the HLB range of 4-6 are W/0 emulsifiers, 7-9 are wetting agents, 8-10 are 0/W emulsifiers, 13-15 are detergents and 10-18 are solubilizers. The HLB system is a useful guide, but in practise, applications are not simple. For example, naturally occurring surfactants will modify the HLB, especially if considerable quantities are present, as already has been pointed out in Section III B.

The results of straight addition of 0.1% of an HLB to separations with Area B and Hole 11 tar sands are shown in Figure 7-37. Only small differences were observed with Area B. In general, the higher HLB of 18, tended to show an increase in oil recovery and solids in the froth and gave less oil associated with the sand. Results with a lean Hole II tar sand were poorer than the no additive separation.

When pH control was used with a full HLB series and a Hole 11 tar sand, small general trends were observed, increased oil recovery with increasing HLB. What appeared real was the maxima and minima that frequently occur in demulsification. The effect of concentration was only explored enough to indicate that maxima occur like those with caustic.

As the tar sands already contain the addition of organic chemicals, appreciable quantities of naturally occurring surfactants, the addition of organic chemicals will modify the action of these surfactants. A simplified explanation of extractability results in proposed mechanisms is illustrated in Table 7-16. However, small quantities of organic surfactant with inorganic agents may improve froth quality, reduce water and solid contaminants, as well as achieve minor improvements in oil recovery.

7-15 Chelating-Complexing

Eleven different chelating and complexing additives specific for calcium and magnesium ions and available off the shelf were evaluated in these studies. Unit Feed - Run No. 6 and Intermediate tar sands were separated with these additives as well as with sodium hydroxide in mixing to adjust the pH to about 9.5. Additives at two different levels of concentration, i.e. 0.005% and 0.05% were used in mixing. The results are summarized in the Appendix.

Oil recovery is plotted as a function of zeta potential of fine solids, Figure 7-38 and 7-39, and specific conductance of the separation water phase, Figures 7-40 and 7-41. In general, the data is reasonably consistent. The patterns do not appear to have any significant importance. It may be concluded again that zeta potential and specific conductance are not sensitive parameters of processability, and are related more to other properties such as how dispersed the system is and what is the ionized salt content. The inter-relationship of these two properties, for this study, was shown in Section 4.

The water to oil and solid to oil ratios are plotted as a function of oil recoveries for two levels of addition in Figures 7-42 and 7-43. It can be seen from Figure 7-42, that at low con-

Table 7-15

1963 Exploratory Data on the Effect of Surfactant Class Base Case : Hole 11 Lean (7.5% Oil) Plus NaOH/NaTPP (0.5/1.0 lbs per ton) at an Oil Rec. of 82%

Base Case: Hole 11 Lean (7.5% Oil) Plus NaOH/NaTPP (0.5/1.0 lbs per ton) at an Oil Rec. of 82%

Class	Chemicals Tested (0.1%)	Oil Rec. zz%
1. Nonionic	- HLB (Chemical Structure)	(See Figure)
	- Pluoronics (M, Wt,)	+6
	- Oil (Pine)	+8
2. Anionic	- Cresylic Acid	+7
	- Sod, Oxalate	+10
3. Cationic	- Ethylene Diamine	+4
4. Amphoteric	- Disodium Ethylene Tetra-Acetate Diamine	+10
5. Polymeric	- Sodium Carboxy Methyl Cellulose	-10
6. Fluorocompounds	- Perfluorohexane	-1
7. Silicones	- Antifoam "A"	-20

Table 7-16

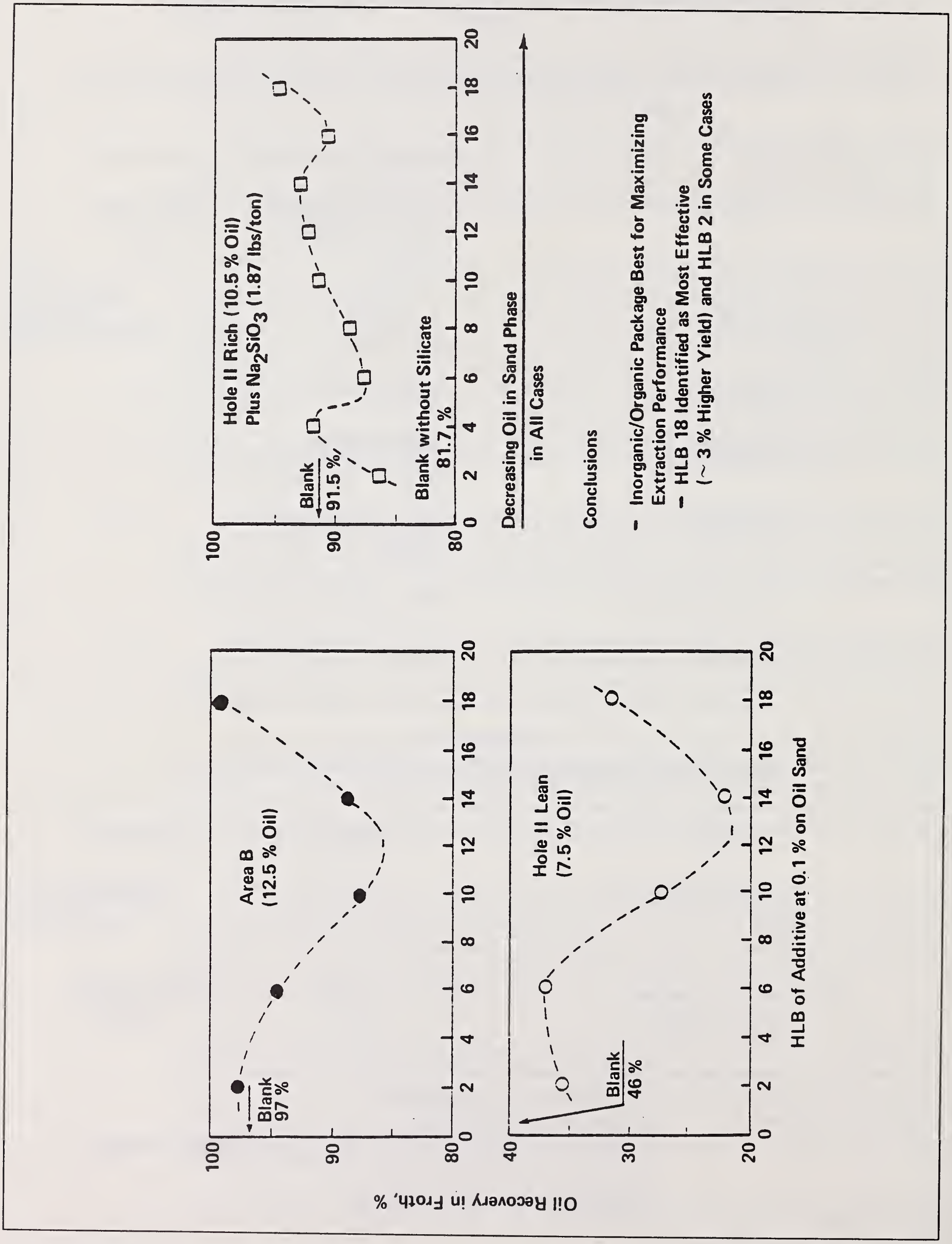
Simplified Explanation of Extractability Results (Without Inorganic Additives)

Surfactant	HLB Range	Function(1)
Naturally Occurring(2) acid	12-14(3)	Emulsification
Plus		
HLB 18 of Additive	15-16(4)	Dispersion(5)
HLB 2 of Additive	7-8(4)	Wetting(5)(6)

Assumptions (1) Normally assigned to an HLB range
(2) Contributes to poor extractability
(3) Derived from poorest results
(4) Blend of equal HLB contributions due to excess use of HLB additive
(5) Results in improved separations
(6) Effect nullified by inorganic agents

Figure 7-37

Data on the Effect of HLB Additives (Pot Extractions)



Conclusions

- Inorganic/Organic Package Best for Maximizing Extraction Performance
- HLB 18 Identified as Most Effective (~ 3 % Higher Yield) and HLB 2 in Some Cases

centrations little or no effect on the water content is observed. However, in the lower plot, Versenol 120 is shown to reduce the solids to oil ratio compared to other complexing agents.

At higher concentrations, Figure 7-43, a divergence occurred between the various additives both in water to oil and solids to oil ratios. There does not seem to be any definite pattern between the different additives in which one additive will reduce the water to oil as well as the solids to oil ratio at the same time. Plotting these two ratios as a function of each other, in Figure 7-44, showed that certain additives that tend to reduce the solids, increase the water. Whereas other additives that reduce water do not decrease the solids.

The overall picture of these additive studies is that the effect of additives in low concentrations of 0.005 wt% on tar sands is not significant. In higher concentrations of 0.05 wt%, effects are observed on froth quality, but no significant change is observed in oil recovery. Measured in the optimum range of the pH, i.e., 9.5. Thus the prospects of utilizing a chelating or complexing agent would be more concerned with reducing froth contaminants in separation than improving oil recovery.

7-16 Summary

These studies show that the addition of chelating or complexing agents in separations conducted at about 9.5 pH (adjusted by simultaneous sodium hydroxide addition) had little effect upon oil recovery. However, significant differences have been observed in both water and solids to oil ratios in the froth. These differences appear to be specific to a particular additive used and no general correlation can be drawn. The small differences observed, and the high cost of these organic complexing additives, do not show the use of these types of additives to be attractive. Admixed with certain chemical inorganic additives such as silicate and/or phosphate, these complexing additives may contribute in small concentrations in the control of low contaminant levels in the froth. However, further work and economic evaluation is clearly indicated before this suggestion has any real basis in fact.

Some of the more important findings from these studies are:

- pH adjustment by the addition of caustic or sodium salts of weak acids in mixing gave higher oil recovery and lower water and solids in the froth product with most tar sands evaluated.
- Good quality tar sands (pH 8-9) after storage at ambient temperatures over a long period, result in low pH values, and exhibit poor processability. When pH was adjusted to alkaline conditions with NaOH, good processability is regained; a readily reversible phenomenon.
- Some poor quality tar sands react satisfactorily with addition of sodium hydroxide and other salts, but other tar sands do not.
- Sodium phosphates and also silicates were found to be the best conditioning agents at 0-6 pound/ton for poorer quality tar sands.
- Sodium Silicate with SiO_2:Na_2O moduli and particularly sodium phosphates with low Na:P and O:P ratios are the preferered pH additives, other than caustic for low cost.
- The beneficial effect of sodium silicate was subsequently demonstrated in the bench unit with hole 21A tar sand. The oil recovery increased from about 20% to about 90%.
- The highest oil recovery and best froth quality were obtained at an optimum pH for a given tar sand. (Although laboratory standard extraction conditions are not necessarily optimum.)
- The optimum pH of the separation water phase was found to be about 9 and varied slightly (± 1pH) with different tar sands and with different additives, and appeared to be affected by the ionic strength of the water phase.
- Organic surfactant additions in separations have indicated that only anionics chelatesand nonionics are effective. The improvements, however, are small, which may reflect the large amount of polar surfactant components already present in the tar sands.

- Utilizing these naturally occurring surfactants by suitable pH control and chemical modification appears to be the best route to better operations.
- Good quality tar sand (pH 8-9) after storage at ambient temperatures over a long period result in low pH values, and exhibit poor processability. pH is readily adjusted to alkaline conditions with NaOH and good processability is regained, a readily reversible phenomenon.

Figure 7-38

Processability as a Function of Zeta Potential (Unit Feed - Run No.6 Tar Sand)

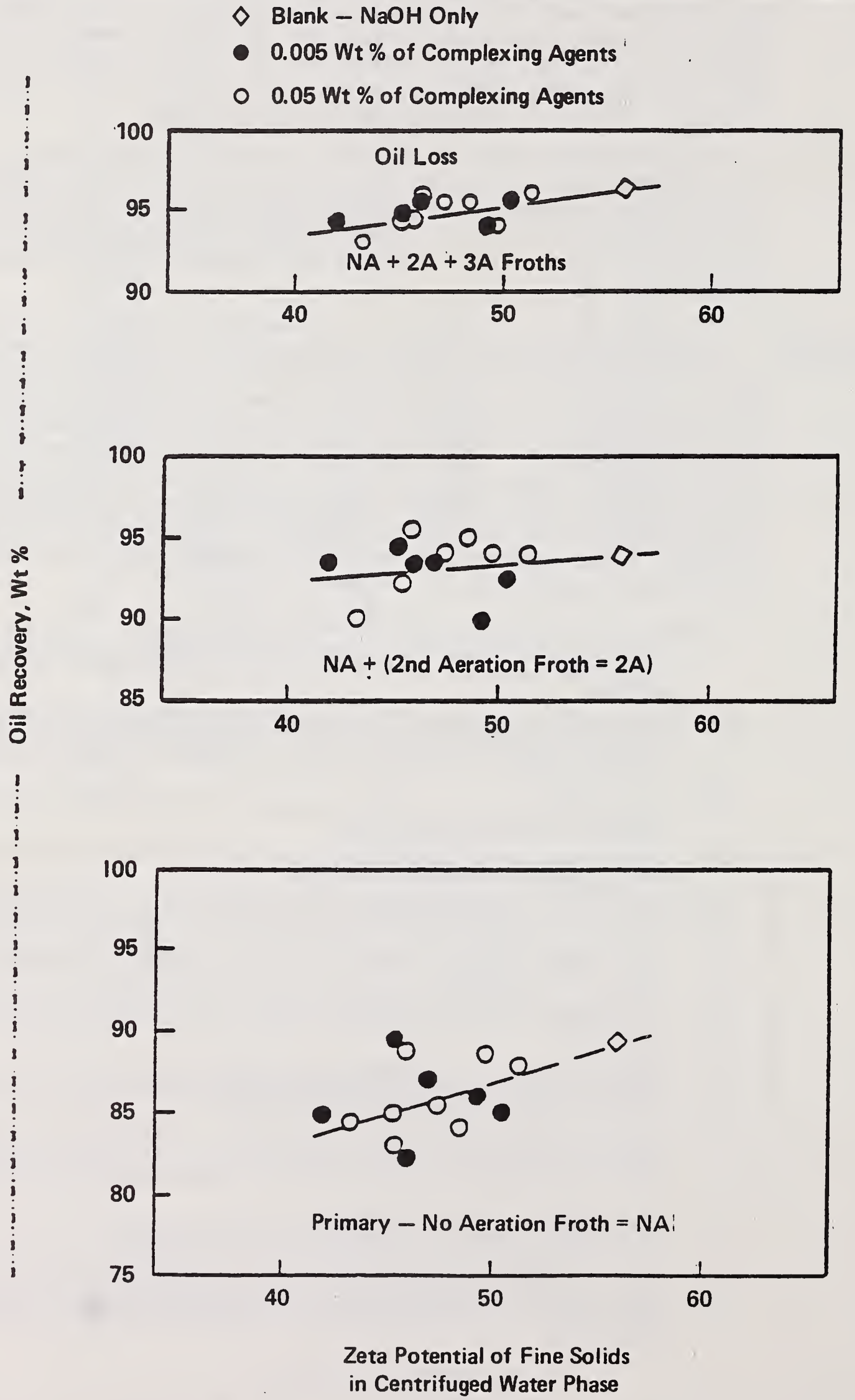


Figure 7-39

Processability as a Function of Zeta Potential in Distilled Water (Unit Feed - Run No.6 Tar Sand)

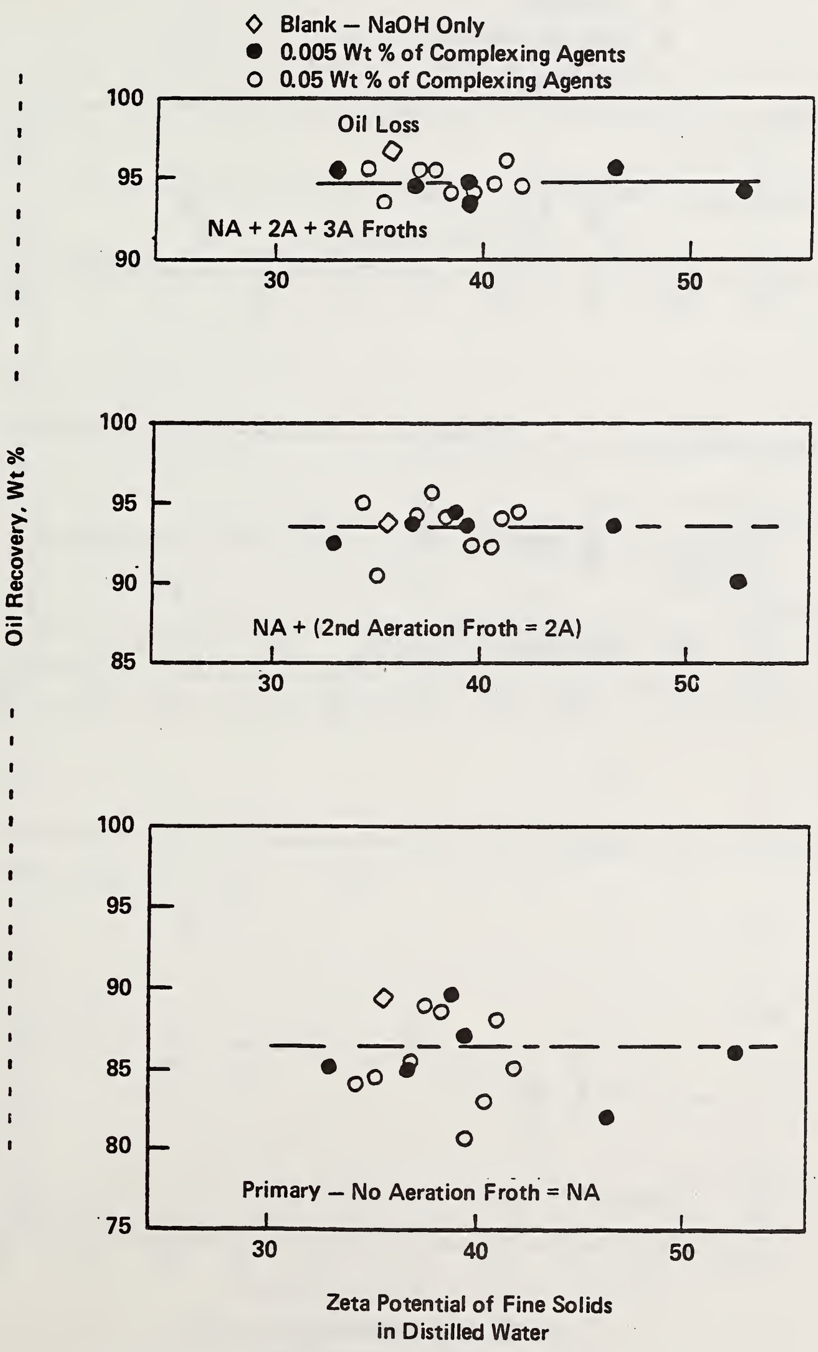


Figure 7-40

Processability with Complexing Agent Additions (Unit Feed - Run No.6 Tar Sand)

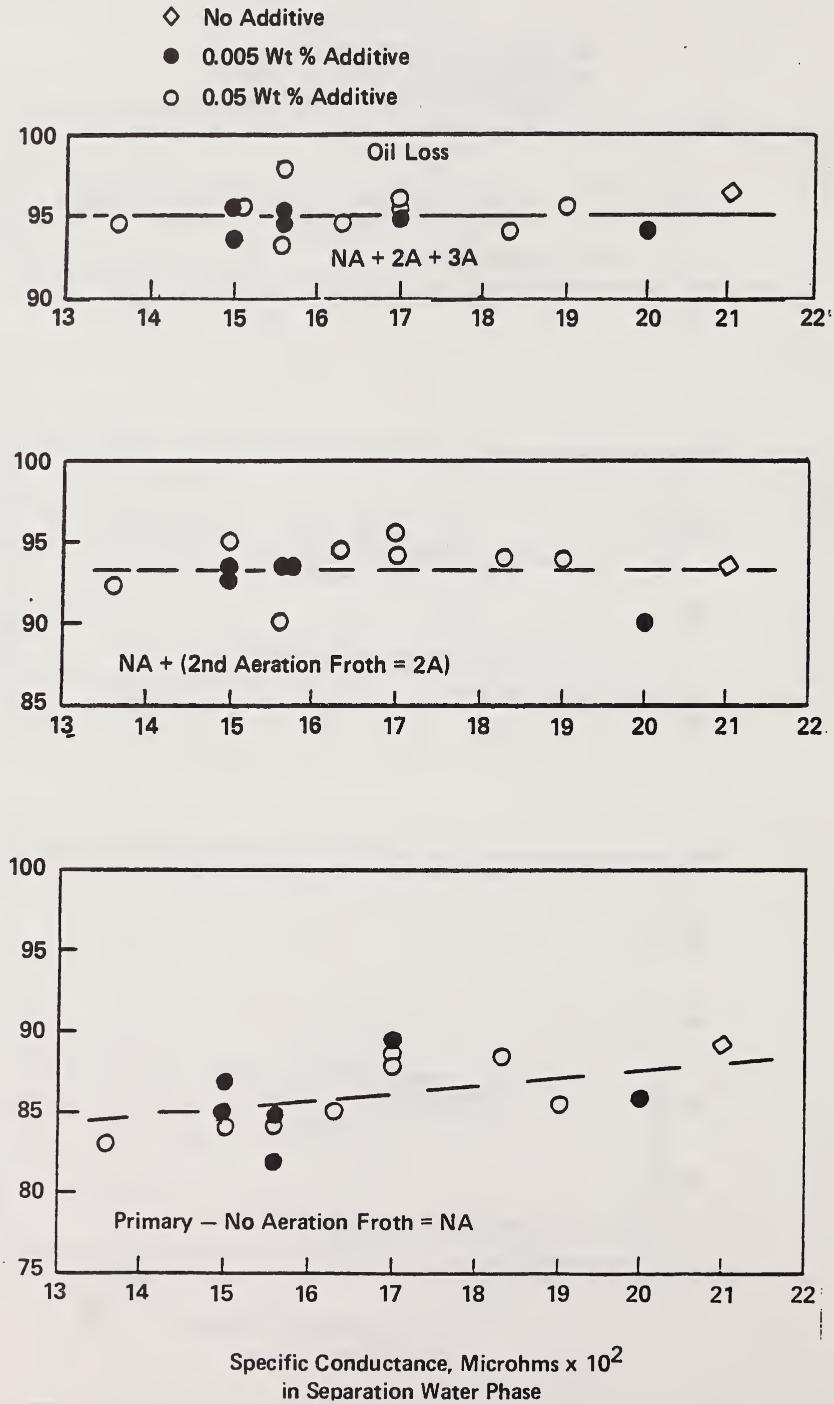


Figure 7-41

Zeta Potential - Specific Conductance Relationship at 9.3-10.0 pH

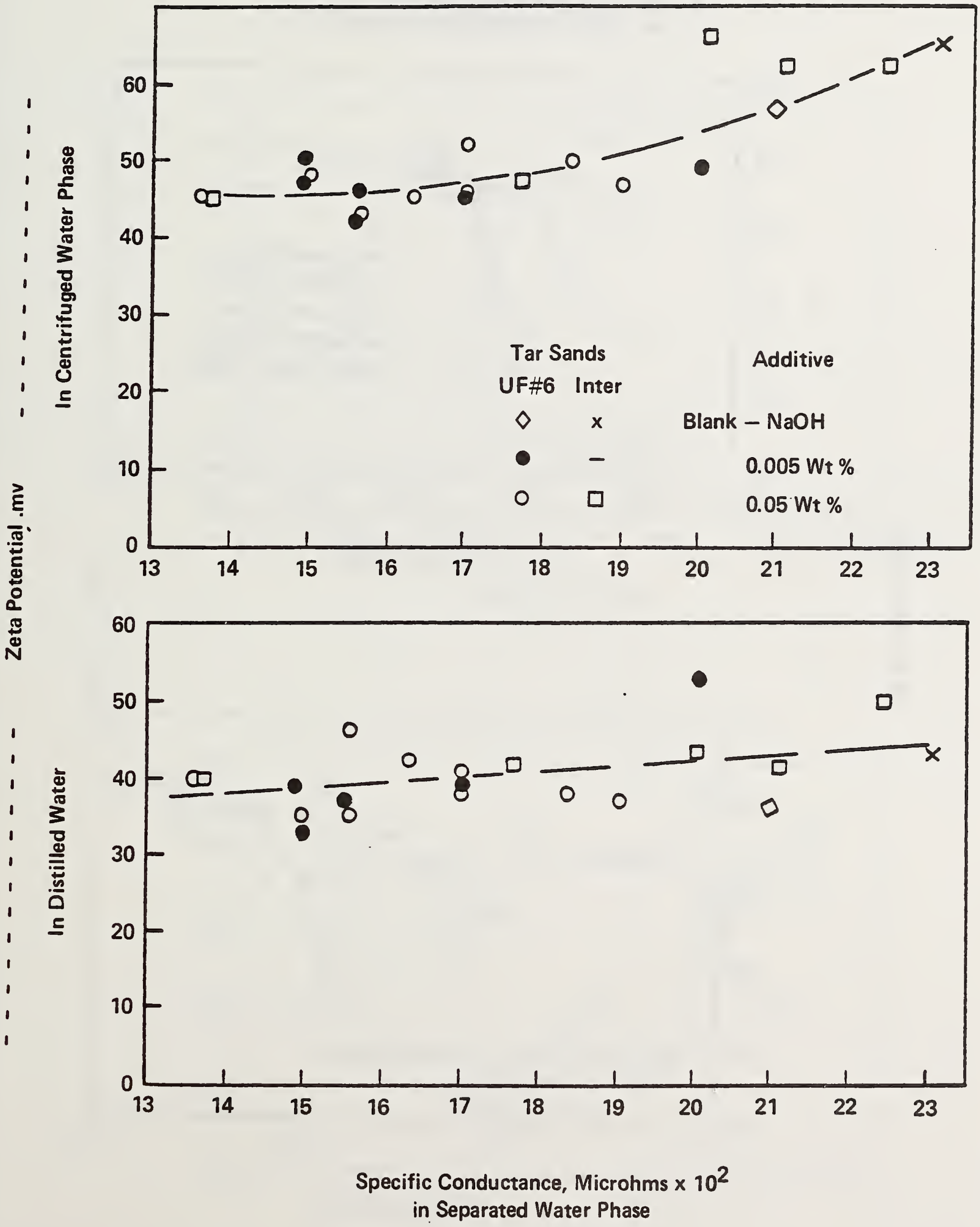


Figure 7-42

Processability with Complexing Additives (0.005 Wt % on Tar Sands) (Unit Feed - Run No.6)

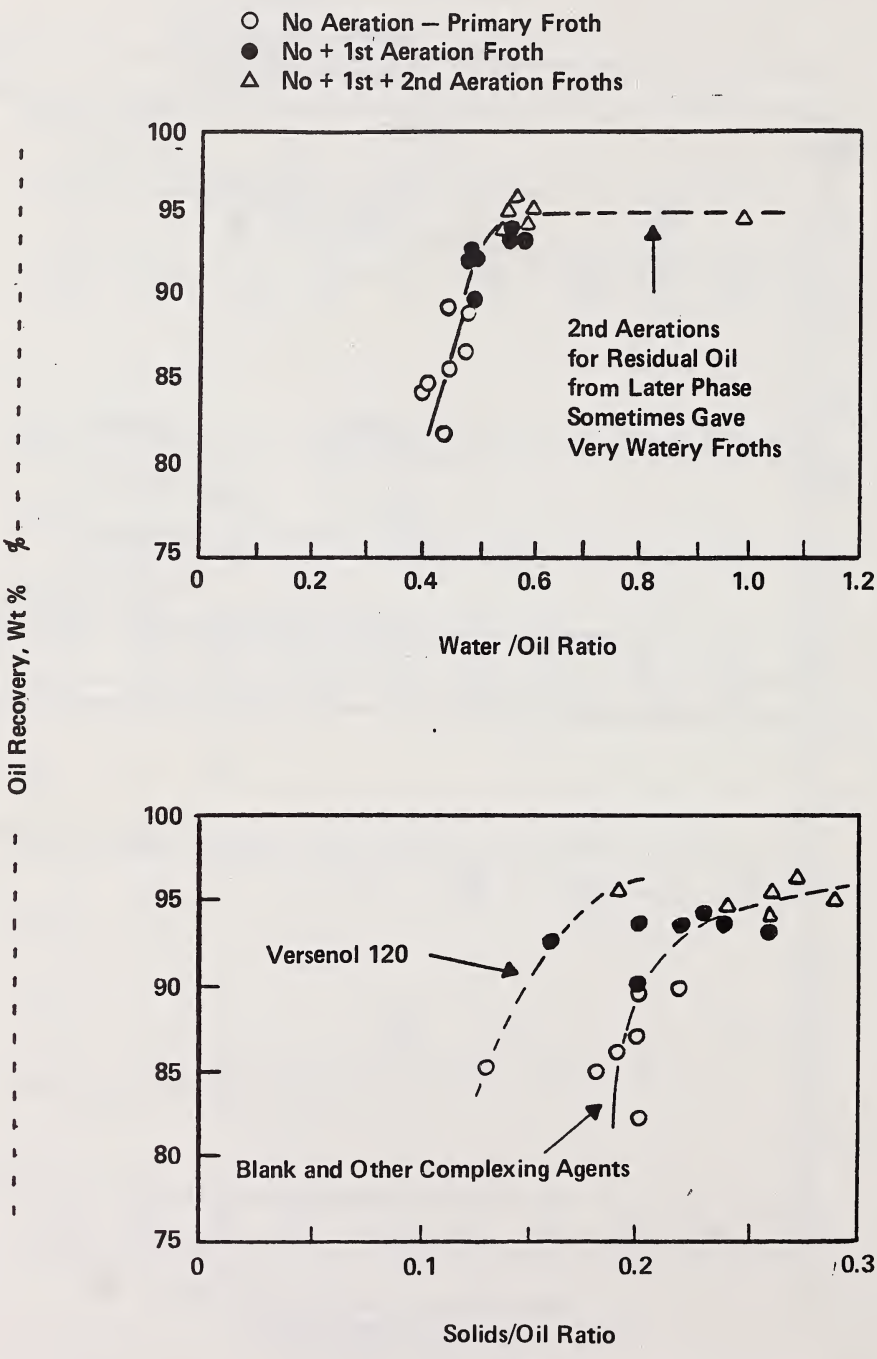


Figure 7-43

Processability with Complexing Additives (0.05 Wt % on Tar Sands) (Unit Feed - Run No.6)

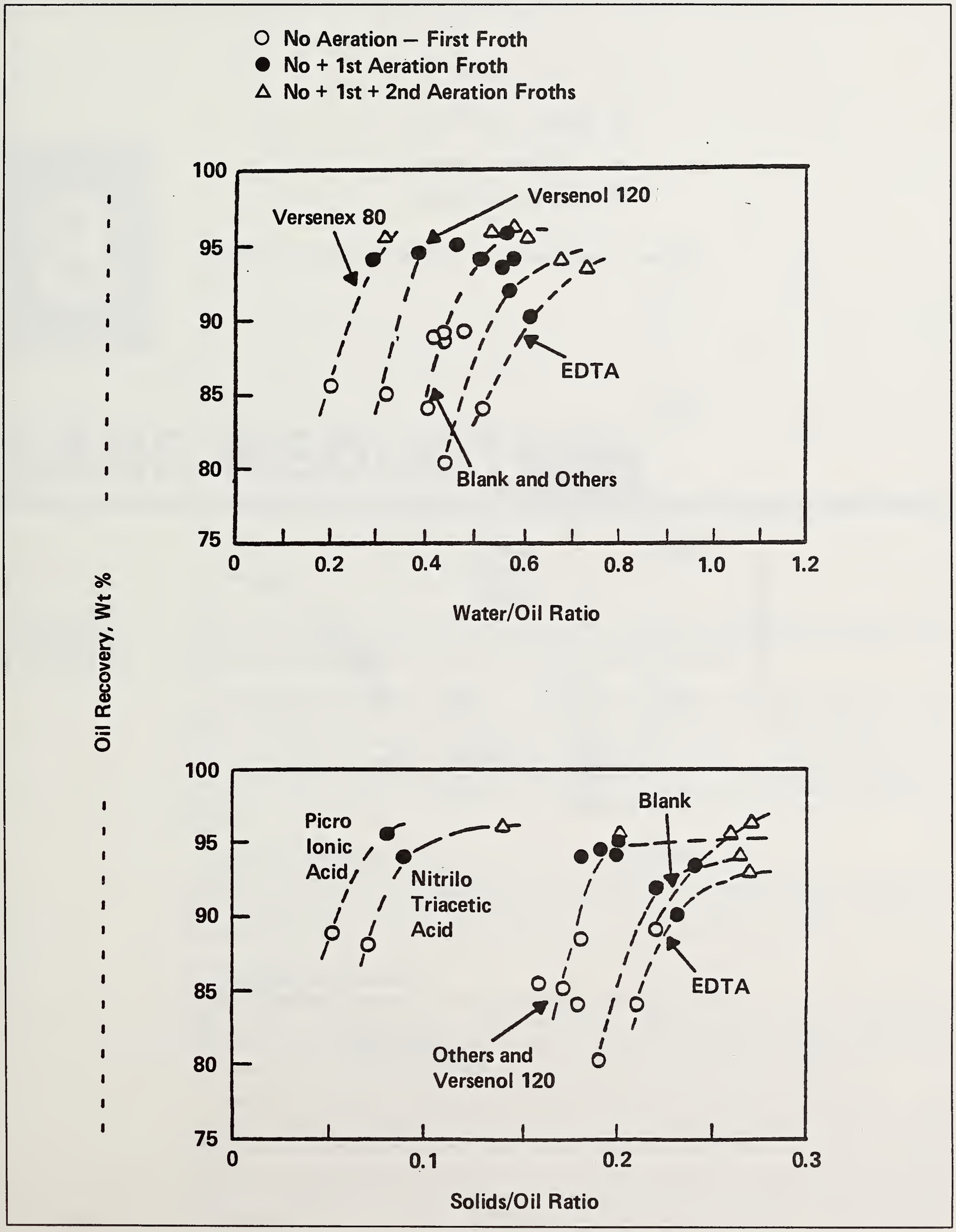
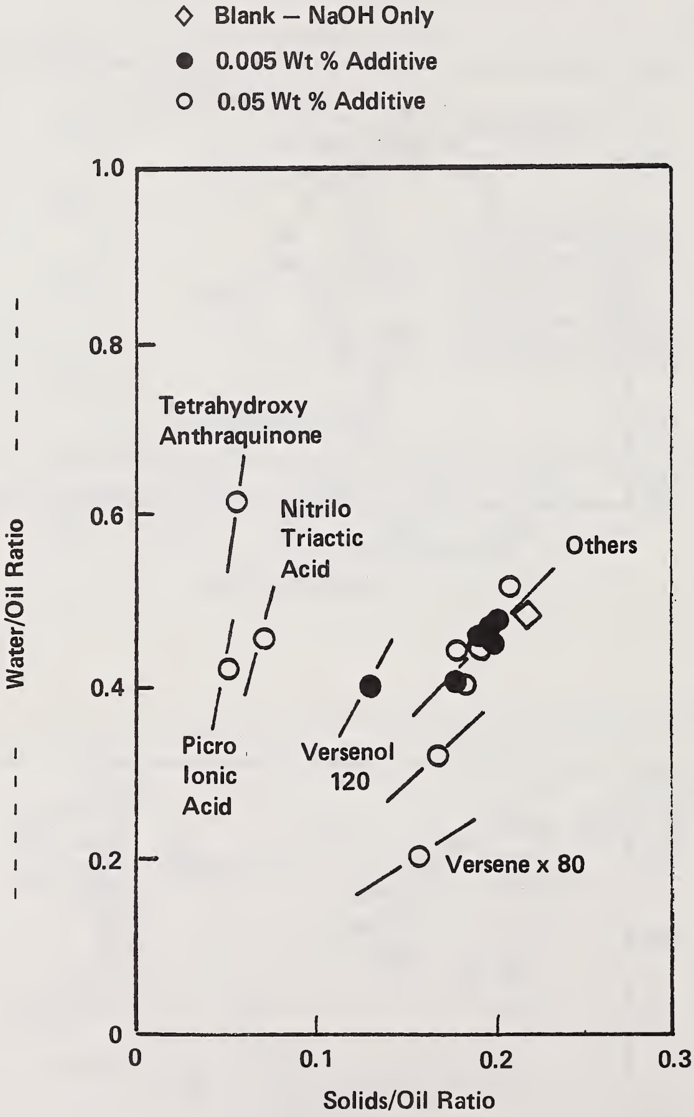


Figure 7-44

Froth Composition with Complexing Agent Addition



8

SAND REDUCTION

8-1 Oil Agglomeration

The concept of the "sand reduction" process is to reduce the sand content of tar sands so that the resulting oil-sand mixture can be fed directly to further processing.

The process is possible as the bitumen is already prevented from wetting the sand by an absorbed film of water in the tar sand structure. Hence mixing with water can thus increase the film thickness and result in substantial sand separation. It has been found that considerable reductions in sand content can be readily achieved by the application of shear in the presence of water. Separation of large quantities of sand occurs rapidly in the initial stages of mixing with water, while the oil forms with some sand, a black plastic mass referred to as "Agglomerate" or "Oil Phase".

Physical separation of the separated sand from agglomerates is then made. The enriched oil phase is processed either by direct coking of the agglomerate or by solvent dilution and separation to remove solids and water contaminants that will be discussed in Section 9. Water is recycled in the process. A general flow plan of this approach is shown in Figure 8-1.

8-1-1 Original Experiments

The ordinal experiments demonstrating the idea of Sand Reduction were carried out at ambient temperature. Some of these oil sands had undergone some aging, Section 11, and hence results do not demonstrate the potentially high oil recoveries that can be obtained. However, these experiments do show some effects of process variables and hence are recorded here.

In the first experiment, a sample of tar sands containing 5 wt% water was mixed with a total of 50 wt% water in a mortar with a pestle for one and a half minutes. The lumps of tar sands were observed to break down immediately and the mass became dispersed in water to a point where the mixture approached uniformity. This occurred in about 5-10 seconds. Further mixing resulted in the appearance of agglomerates, and sand was observed to accumulate in the bottom of the mortar. These agglomerates grew in size with further mixing, forming one large oil phase

Figure 8-1

Sand Reduction

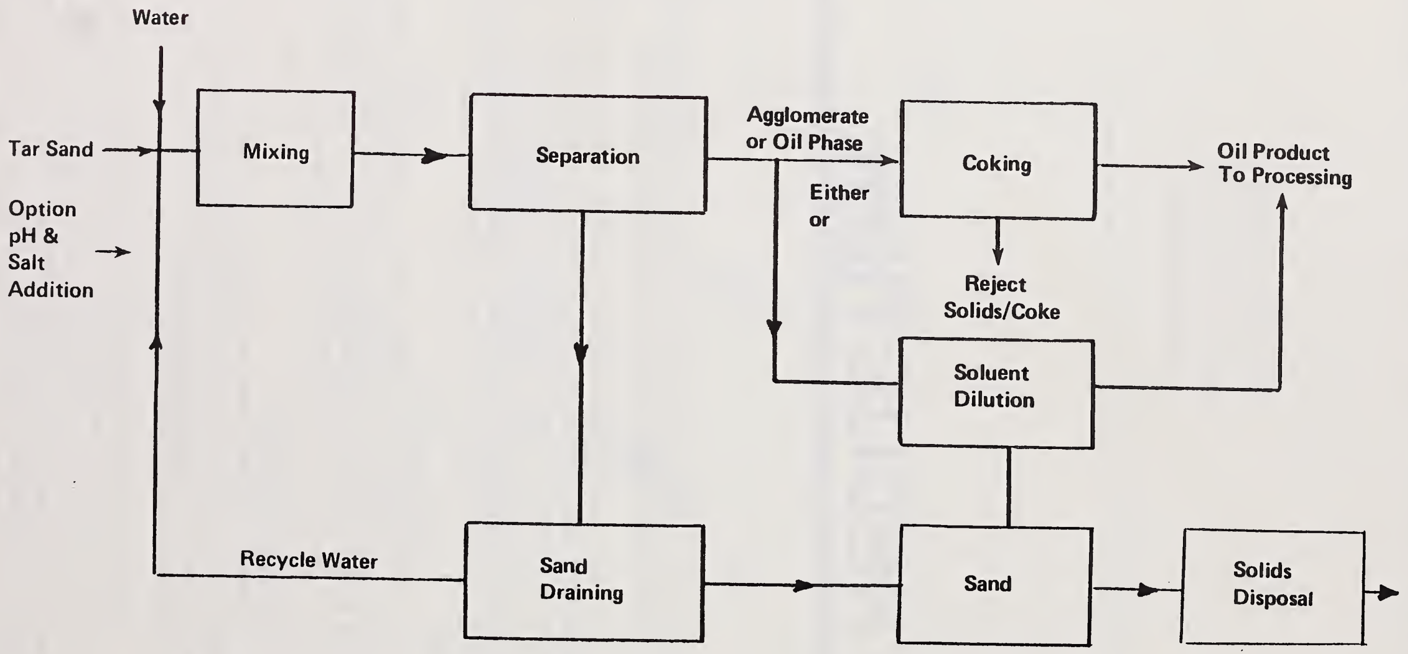


Table 8-1

Original Sand Reduction Experiments (Tar Sand Mixed with Water in a Motar with a Pestle at Room Temperature 100% Oil Recover (Est)

Experiment No.	1	2(1)	3	4		
Tar Sand No.	0	0	2	1		
				1st Pass	2nd Pass(3)	Total(4)
Connate Water, Wt%(5)	5			2	-	-
Total Water in Mixing, Wt%(6)	50	67	52	50	50	100
Mixing Time in Minutes	5	4	5	5	1	6
Dry Sand Recovered, Wt%(6)	73	64	76	37	17	54
Dried Oil Phase Recovered, Wt%(6)	27	36(3)	24	63	46	46
Solids Removed, Wt%(7)	87	76	90	44	20	64

(1) Automatic pestle and mortar
(2) Collected on scraper
(3) Whipped agglomerate in water
(4) Sum of 1st and 2nd passes
(5) Wt% in original Tar Sand Feed
(6) Wt% on Dry Tar Sand Feed
(7) Wt% on Total Solids in Original Tar Sand Feed

Table 8-2

A Minimum Amount of Water is Required in Sand Reduction (Tar Sand No. O contained 5 Wt % Water and 15 Wt % Oil

Total Water Wt% on Tar Sands (Dry Basis)	Time in Seconds for Bitumen-Sand Plastic Phase to Completely Separate
30	-(1)
40	90(2)
50	60
75	50
100	45
150	35
200	30

(1) Mixing time was extended to five minutes - intimate slurry obtained.
(2) Some separation occurred, but obviously not enough water.

above the separated sand. This agglomerate was made to adhere to the pestle, and recovery was achieved by removing the pestle from the mortar. The remaining wet sand was essentially oil free. It was found that up to 85-90 wt% of the solids in the original tar sands were removed, leaving a recovered oil phase containing approximately 60 wt% of oil. The oil recovery was high at approx. 98%. The simplicity and speed of the separation was surprising.

Other experiments were carried out in an automatic pestle and mortar with mixing for four minutes at room temperature, Table 8-1. The recovered oil phase, collected by the automatic scraper, had the following composition: 19 wt% water, 36 wt% oil, and 45 wt% sand. The "sand reduction", defined as the solids removed expressed as the weight percent of the solids originally present in the tar sand (dry basis), was found to be 64 wt%. It was concluded that this sample of oil sand had undergone some aging or drying out, and the equipment was only partially effective in conducting the process.

It was thought that water washing of the extracted oil phase might reduce the solids content further. This was tried with the extracted oil phase in a manual mixing operation with 2 lots of 50 wt% water that were added in two successive mixings for a total of 100 wt% water on tar sands. It was found that the first mixing resulted in removal of a further 17 wt% of solids, but very little sand was removed in the subsequent washing of the oil phase with water. The sand reduction had therefore been increased to approximately 80 wt%.

8-1-2 Water in Mixing

A series of mortar and pestle experiments were carried out to study the amount of water required in the mixing operation. The results are shown in Table 8-2. It was found that, when less than 30 wt% of water on tar sands was used in the mixing operation, no separation was achieved even after the extended mixing time of 5 minutes. With 40 wt% water, some separation was achieved. It can be seen from Table 8-2 that the time for the oil phase to separate decreases with increasing amounts of water used in the mixing operation. However, it was observed that with an amount of water greater than 100 wt%, the viscosity of the mixture appeared to decrease and some of the small dispersed oil particles did not readily adhere to the oil phase. These observations indicate that an optimum amount of water is required in mixing.

Additional experiments were carried out to determine this optimum amount of water that is mainly required to effect agglomeration of an oil phase and not Sand Reduction per se. An improved mortar and pestle technique was used in the experiments, that involved a 20 mesh screen submerged in water for the separation of the large oil agglomerates from the free sand and clay suspended in the water phase. This proved to be a remarkably effective method for separating the phases.

The amounts of sand removed by mixing a tar sand with water at room temperature are plotted against the total water used in mixing in Figure 8-2. It can be seen that a minimum total water of 30-40 wt% on tar sands (dry basis) are required for sand to separate, as was previously concluded from the original experiments (Table 8-2). The water added below this level was taken up in the structure, presumably swelling the films of water around the sand; the result was a "porridge-like mass".

Larger water additions, i.e. 40-60 wt%, resulted in a substantial release of clean sand. Apparently, the excess water over the minimum 40 wt% is enough for the existence of both dispersed oil and sand phases. However, less water is required at higher temperatures for sand to start to separate. Increasing the total water in mixing in the range 50-100 wt% resulted in a maximum sand removal of 74 wt%; virtually no oil was lost in the sand product. In this range, sand reduction and oil agglomeration appeared to be maximized.

Increasing the total water, beyond 150 wt% appeared to have a beneficial washing effect on the agglomerates, and good agglomeration was achieved, giving about constant sand reduction even with 300 wt% total water in mixing. The benefit of washing agglomerates was observed previously and pointed out in the description of the preliminary experiments. Beyond 300 wt% total water, a poor oil recovery through poor agglomeration was obtained with small oil particles passing through the 20 U.S. mesh sieve used in the separation. Clearly, the more water used, the

Figure 8-2

An Optimum Amount of Water Gave Greatest Sand Reduction in Mixing

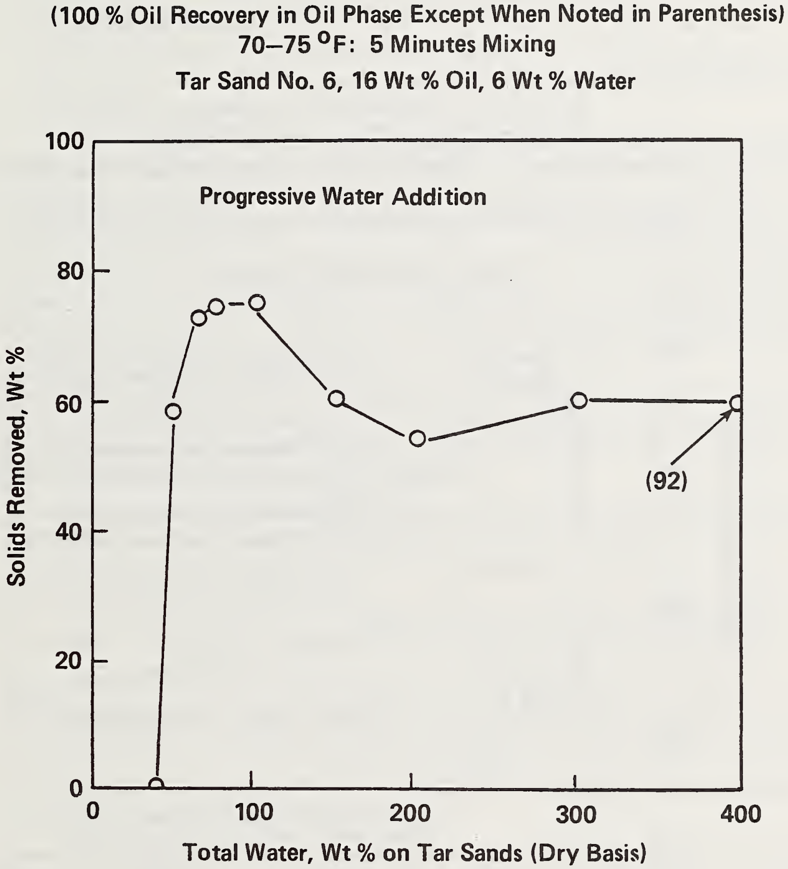
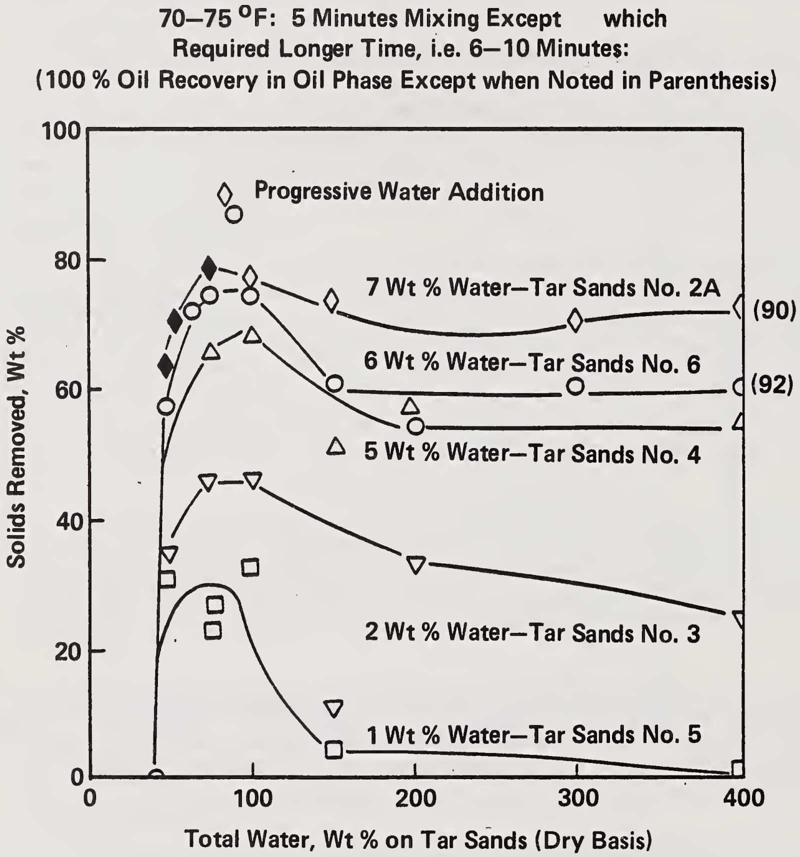


Figure 8-3

Effect of Tar Sands Water Content on Sand Reduction



less effective is shearing in agglomerating the oil phases. Conversely, longer mixing time would be needed to achieve a good result.

In general, these data show the existence of an optimum amount of water for mixing to effect good sand reduction and oil agglomeration. In one experiment shown by the square point in Figure 8-2, the water was added in small increments during the mixing operation; this resulted in a markedly higher level of sand removal. This indicates that an optimum shear/water usage is needed to maximize sand reduction.

8-1-3 Connate Water

The water content of the tar sands can vary from near 0 to about 20 wt%. Most recorded values are about 1-7 wt%. In any commercial process, mined tar sands of different connate water will have to be processed.

Thus, a similar set of experiments, as discussed above, was carried out using tar sands with different water content. The results are plotted in Figure 8-3. Although, some tar sand feed qualities e.g. aging, by "drying out" may have occurred, optimum sand reduction was obtained with each type of feed in the same range of total water and mixing time. However, it will be noted that much less sand was removed from tar sands with low connate water. Progressive water addition gave better results than simply addition with Tar Sand 2A as well as with Tar Sand No 6. The solids removed are a direct function of the connate water of the tar sands, see lower curve in Figure 8-4. Alternately, the conditions can improve sand reduction from the lower connate tar sands that need relatively more shear to release solids.

These optima describe a curve, Figure 8-4, of increasing solids removed with increasing connate water at these fixed separation conditions from these stored oil sands that presumably had undergone some drying out. However the same general trend was observed with fresher tar sands and sand reduction was substantially greater.

This comparison indicates that an ongoing commercial operation on freshly mined oil sands will perform better than is indicated by these early results and studies.

8-1-4 Agglomeration Mechanism

It was observed that there are two main mechanisms of "sand reduction" on mixing tar sands with water. The optimum amount of water appeared to be the same in each case.

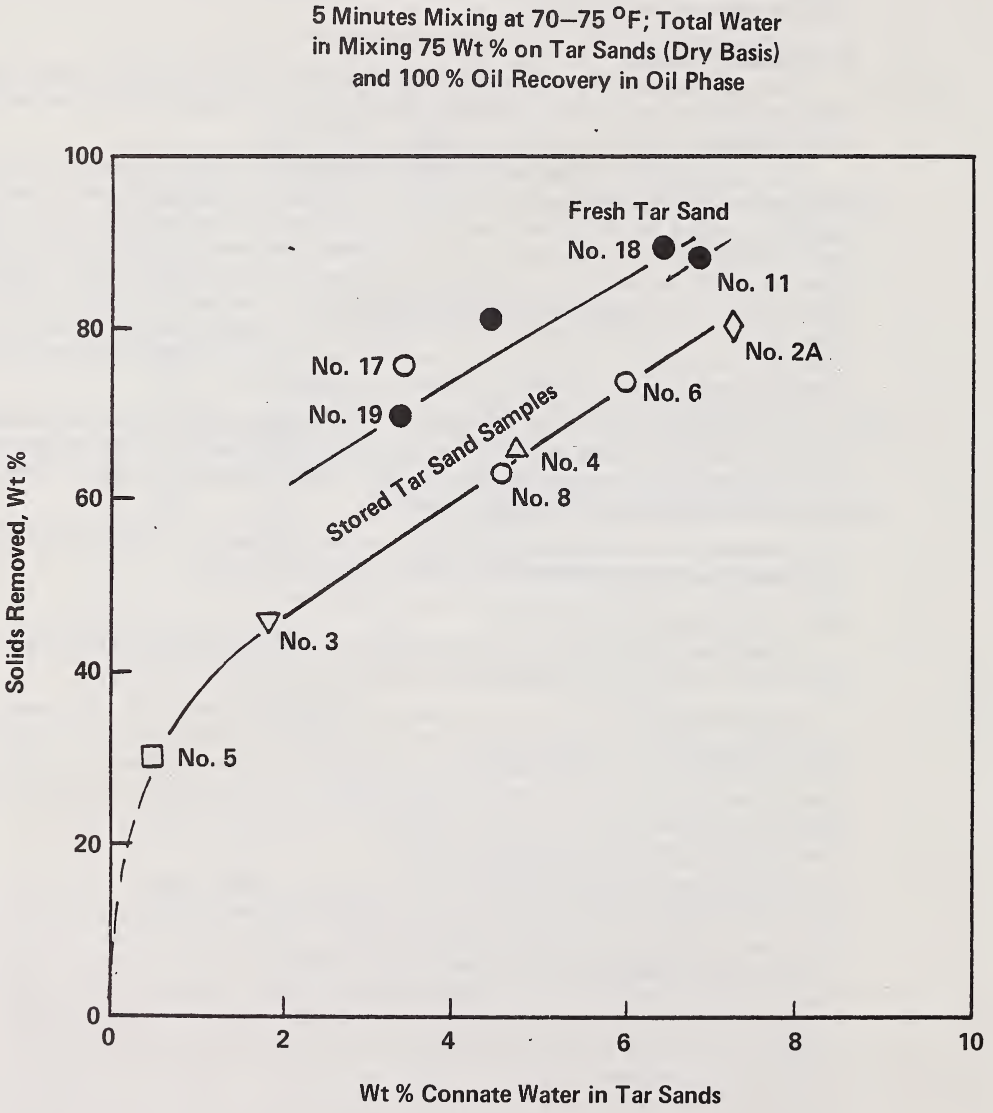
The first mechanism occurs with tar sands containing less than 9 wt% oil or more than 6 wt% connate water. On mixing this type of tar sand with 30-300 wt% water, the structure breaks down in about 5 to 25 seconds under very gentle mixing. The resulting mixture is a dispersion in water of sand and very small oil particles, presumably from the voids between the wet sand particles in the original structure. On further mixing, these oil particles coalesce, together with some sand, to form an oil phase; i.e. "agglomeration".

The higher the connate water in the tar sand, the longer the mixing time required to complete "agglomeration" for total oil recovery. In a commercial "sand reduction" operation, mixing with water to effect disintegration would be short e.g., less than one minute. Further the best mixing for the remainder of the time would require a fraction specific for bitumen "agglomeration". The second mechanism occurs with tar sands containing more than 9 wt% oil or less than 5 wt% connate water. On mixing this type of tar sands with water for less than one minute, small lumps are formed and not the discrete particles of oil and sand as in the first mechanism. Little or no free sand separates at this time. Further mixing results in release of sand from these aggregates. The net result is similar to that of the first mechanism after about 5 minutes of mixing in which clean wet sand and an oil phase were obtained. However, the sand removal tends to be less by this mechanism under the conditions used, but would presumably improve with more shear. The main mixing operation in a commercial application of this process would require that this type of tar sands be beaten or kneaded with a critical or optimum amount of water to effect a maximum Sand Reduction at high oil recovers.

When the tar sands contained approximately 9 wt% oil and 6 wt% water, then an intermediate mechanism was observed. The aggregates from which sand was lost also behaved as nuclei on which the very small oil particles coalesced readily; this resulted in very good ag-

Figure 8-4

Tar Sand Storage Decreases Potential for Sand Reduction



glomeration. The same mechanism applies to lower grades of oil sands with "agglomerate recycle".

8-1-5 Temperature

The results of studies with high water content tar sands (6 wt%) on the effect of temperature are plotted in Figure 8-5. Just above 32°F the breakdown of the tar sands occurred readily on mixing. Agglomeration was poor up to 40°F as some oil passed through the 20 mesh sieve with the sand. At higher temperatures up to about 60°F, agglomeration occurred, but some oil particles were still lost with the wet sand phase. A factor that reduces agglomeration at low temperatures is the high oil viscosity and low adhesion. Thus, to achieve adequate agglomeration, longer mixing times are required at lower temperatures.

It was observed under a microscope that some very small solids in the form of a skin were adhering to these very small bitumen particles. As solids are e.g. "clay", in general, negatively charged, then the reluctance of these small particles to coalesce may be due to charge effects. If this is so, then the addition, of chemicals would aid agglomeration. Preliminary experiments with addition of sodium salts showed improvements in adhesion of these bitumen particles.

High oil recoveries (good agglomeration) and good sand reduction were obtained at temperatures of 60 to 90°F. At higher temperatures, i.e. above about 100°F, the reduced viscosity of the oil phase resulted in fluid agglomerates of poor stability. Also the oil phase became very tacky in the higher temperature range (90-150°F) and separations were difficult as the bitumen tended to float on the water phase and to stick to the sides of the mortar above the water line. Cooling of the mixture by quenching with cold water before screening under water was necessary to the experimental technique. Further, it was found that if the temperature of screening was less than 70°F, very little or no fouling of the submerged screen occurred.

Sand reduction with tar sands low (approx. 1%) in connate water content that may have occurred by dehydration in storage, was found to increase about linearly with temperature, Figure 8-6. It is thought that the decrease in viscosity of the oil with increasing temperature enabled more solids rewetting and sand release from the structure at higher temperature.

(a) Flexibility in Sand Reduction

It has been shown that mixing tar sands with a critical amount of water at ambient temperatures in a one-stage operation can result in removal of a large amount of clean sand, particularly with tar sands of high water content. This approach gives relatively low sand reduction with tar sands low in water content. However, increasing the temperature of mixing with tar sands low in connate water has been found to increase sand removal.

The comparison shown in Table 8-3 illustrates how the effect of temperature provides flexibility in the process to handle tar sands low in water content. It can be seen that the progressive lowering of temperature effects good sand release and subsequent good agglomeration at lower temperatures. The best sand reduction obtained in these experiments was 80 wt%.

Hence, optimizing temperature with progressive addition of water to maximize shear can achieve optimum results.

8-1-6 Clay/Water Recycle

Mortar and pestle studies with lumps of clay added to the tar sand feed have indicated a greater clay tolerance in sand reduction than in the hot water separation process. This comparison is shown in Figure 8-7, although it should be noted that some of the oil lost to sludge, not shown, in the hot water separation process can be recovered by aeration in subsequent secondary processing.

These experiments indicate that amounts of clay up to approximately 25 wt% on tar sands may be tolerated in the feed, without any significant effect on oil recovery in the sand reduction process. This effect was confirmed in continuous process demonstrations using a pug mill/rotating submerged screen separator, Figure 8-7. However, it is interesting that with amounts greater than 25 wt%, poor agglomeration occurred. The oil that passed through the 20 mesh screen was retained with the sand on the 325 mesh screen. The recovered clay (i.e. less than 325) did not contain any oil. It was observed that at these higher clay contents the oil tended to float. Al-

Figure 8-5

Sand Reduction and Oil Recovery Are Optimized by Operating Temperature with a High Water Content Tar Sands 75 Wt % Total Water : 5 Minutes Mixing

(Oil Recoveries Are Shown in Parenthesis)

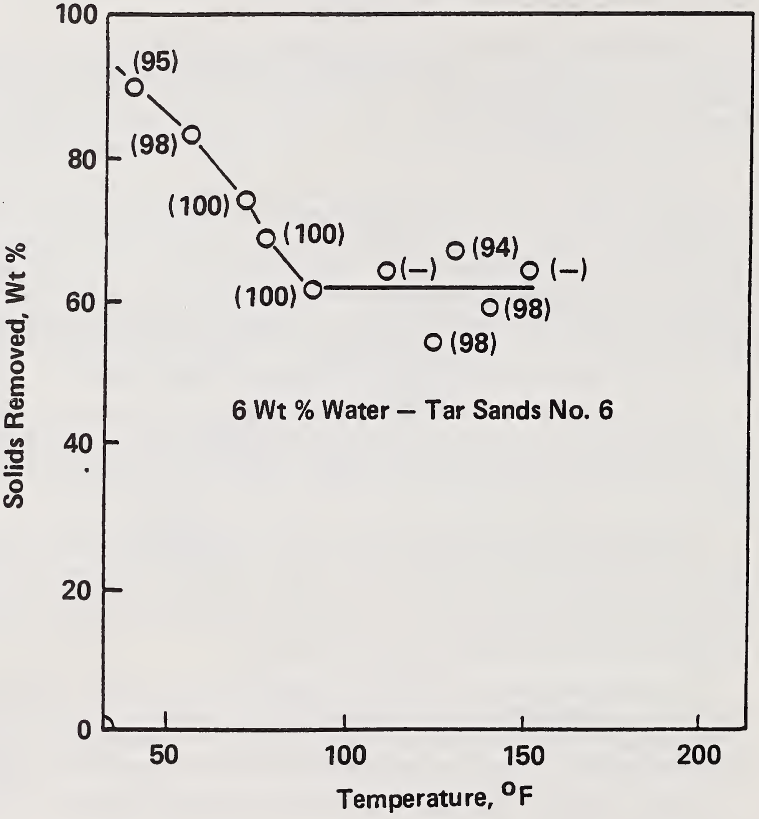
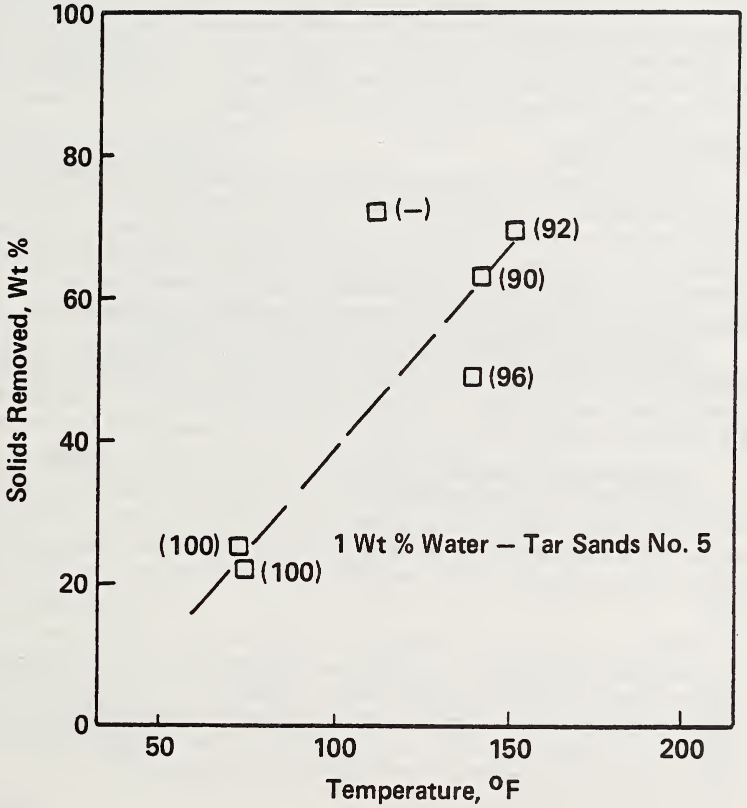


Figure 8-6

Effect of Temperature on Sand Reduction with a Low Water Content Tar Sands 75 Wt % Total Water : 5 Minutes Mixing

(Oil Recoveries Are Shown in Parenthesis)



though probably not too practical, it is conceivable that this could be used as a method of separation, eg. brine/aeration, to achieve high oil recovers.

It was thought that the effect of clay in causing poor agglomeration was physical. The clay formed a skin around the oil phase, hence, the more clay, then the greater the surface area of oil-clay and the smaller the oil particle size. However, this mechanism is not consistent with the shape of the correlated data in Figure 8-7.

The addition of 25 wt% sand or clay (325-fines) to Area B tar sand had surprisingly little effect on sand reduction or oil recovery in continuous pilot plant demonstrations carried out on site at Mildred Lake, Figure 8-8. The oil contents of the resulting blends ranged from 9.0 to 9.5% that indicates it is not low oil content phase of tar sands which is responsible for poor processability. The clay in the recycle water (up to 13%) did not result in an increase in the solids content of the agglomerate, in fact, a slight (but probably insignificant) decrease occurred. The presence of clay in the recycle water increased the oil content of the water stream, eg. 1% at 10% clay, with this oil sand. Since the sand product contained approximately 20% water, part of the oil content of the sand (in some cases almost all of it) was introduced by the water. Solids reduction was approximately 80% over the entire range of clay levels studied. Oil recoveries were over 96% for all tests but one. The reason for the one low value (87%) was not determined.

8-1-7 Coke Addition

After the original Sand Reduction studies on tar sand separation using shear with water at ambient temperatures, it was thought that a carrier for the oil having a "hydrophobic" surface might improve the effect, displacing more sand from the agglomerate. This was tried using various forms of carbon. It was observed that the carbon added goes into the oil phase or agglomerate, and appeared to behave as a carrier for the oil increasing the viscosity of the oil phase and acting as a scavenger for small oil particles, hence aiding agglomeration.

Some experiments were carried out in which the tar sands were shaken and mixed with different types of coke and water in a glass bottle, (shaking is probably not the best method of mixing). Good sand reduction and agglomeration was achieved. The results are shown in Table 8-4. It was observed that the longer the shaking the larger the agglomerates became.

The advantage of fluid coke addition, that is a possible by-product of subsequent oil processing, with a high water content tar sand was found to be negligible, as illustrated by the mortar and pestle results plotted in Figure 8-9. It should be noted that fluid coke is on the average about the same particle size as the sand. Large additions of coke up to 25 wt% that gave only small improvements in Sand Reduction also resulted in some loss of fluid coke with the sand.

Further experiments were carried out with a low water content tar sand, different temperatures and fluid coke addition. The results are compared with those from experiments without coke in Figure 8-10. It can be seen that the best results with coke addition were obtained at 125°F. The property of the coke to increase the viscosity of the oil phase was found to be very useful at the higher temperatures. Mixing was very clean and agglomeration appeared to be similar to that of the operations at lower temperatures without coke.

8-1-8 Chemical Adjustment

Some preliminary small scale pestle and mortar as well as ball mill studies with poor quality, eg. Hole 11 Area D, tar sands showed polyphosphates to have a significant effect in increasing the rate of agglomeration. This is probably due to the sequestering effect of polyphosphates for deleterious polyvalent ions in aged or oxidized oil sands. Oil recoveries were 90+% with low grade oil sands. Silicate and to a lesser extent carbonate also gave improvements. Separations were best under alkaline conditions that is also optimum for hot water separation.

Further, recycle of either agglomerate, or crude or residue at approximately 10% on oil gave substantial improvements in agglomeration and essentially 95+% oil recovery with half as long mixing times than normally used in the test.

Combined oil recycle and chemical treating can be used to produce lower water/solids agglomerates at higher oil recoveries with low quality oil sands. These types of chemical treatment

Table 8-3

Progressive Lowering of Temperature Gives Good Agglomeration and Sand Reduction (Tar Sand No. 3 contained 2 Wt % Connate Water)

Number of Mixing Stages	1	1	2	2
Type of Temperature Operation				
	Constant	Decreasing		
		Continuously(1)	In Stages(2)	In Stages(3)
Temperature, °F	70	140 - 80	140 and 70	130 and 70
Total Water in Mixing, Wt%	100	100	100	40 - 60
Mixing Time, Minutes	5	5	2-1/2 and 2-1/2	2-1/2 and 2-1/2
Solids Removed, Wt%	45	54	80	77

(1) At a rate of 12° per min. by external cooling
(2) Rapid external cooling between stages
(3) Rapid external cooling between stages, added water at 40°F

Table 8-4

Sand Reduction Experiments with "Carbon" Addition(7) Room Temperature Operations Essentially 100% Oil Recovery in Oil Phase

Type of Mixing	Shaking in a Bottle				Mortar and Pestle	"Hobart" Mixer(5)	
Tar Sands No.	0	0	1	2	2	1	2
Connate Water, Wt%(1)	5	5	2	5	5	2	5
Oil Content, Wt%(1)	15	15	17	15	15	17	15
Operation							
"Carbon", Wt%(1)	76(2)	42(3)	20(3)	100(3)	40(3)	36(3)	40(4)
Total Water, Wt%(1)	142	75	57	80	70	62	60
Mixing Time in Min	5	5	7	7	-	20(6)	6(6)
Results							
Solids Removed, Wt%(1)	73	65	50	63	71	71	67
"Agglomerates", Wt%(1) (Excluding "Carbon")	27	35	50	37	29	29	33

(1) On tar sands (dry basis)
(2) Cocoanut charcoal
(3) Fluid coke
(4) Sarnia breeze
(5) 1000 g charge and cheese cloth separation
(6) Less time required to effect separation
(7) These data may be compared with those of Table

Figure 8-7

Comparison of Effect of Clay on Oil Recovery in Sand Reduction and in Hot Water Separation Process

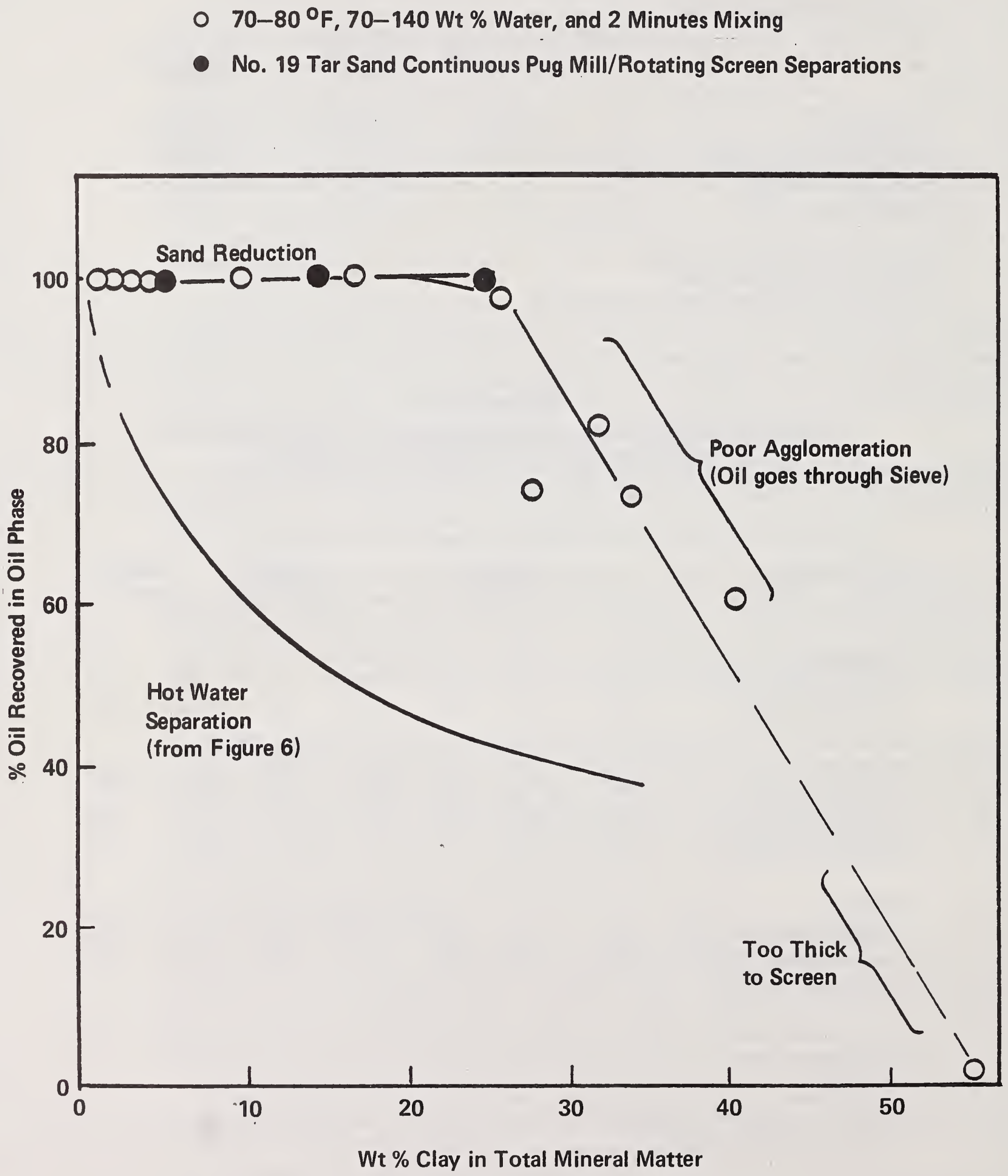


Figure 8-8

Clay in Recycle Water Has Little Effect on Agglomerate Quality

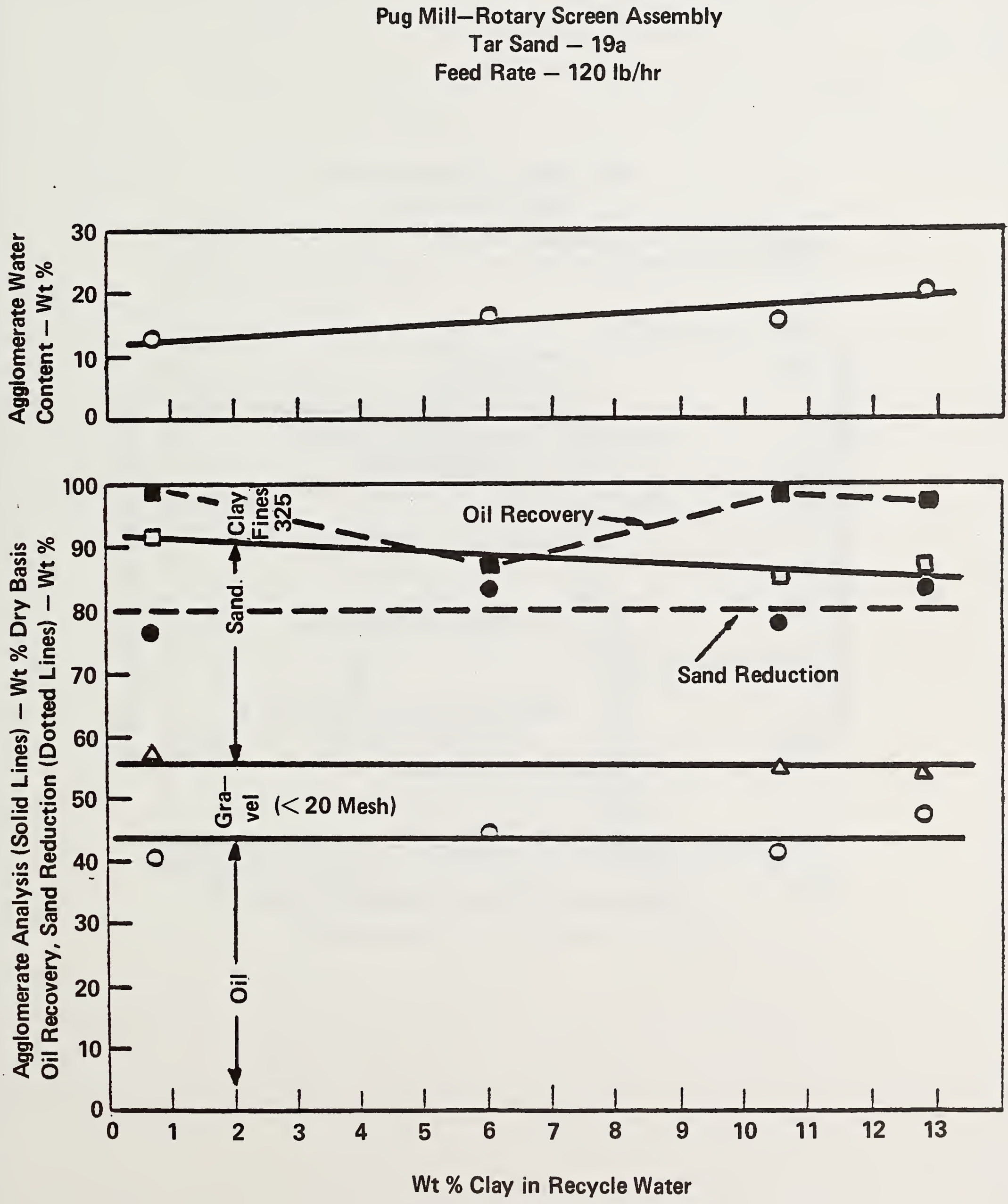


Figure 8-9

Effect of Fluid Coke Addition on Sand Reduction with a High Water Content Tar Sand 70-75 °F 5 Minutes Mixing 100 % Recovery

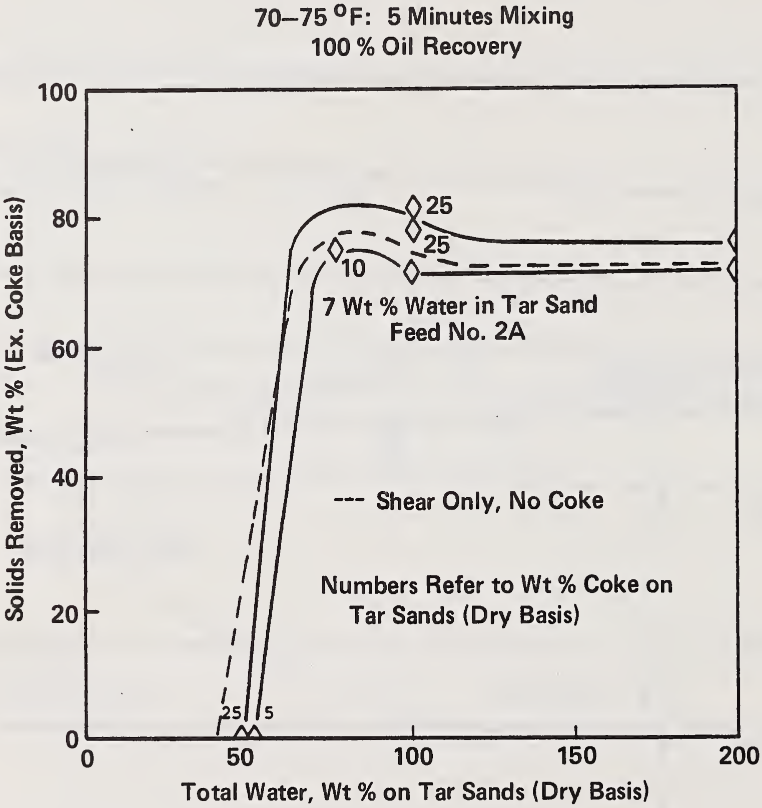
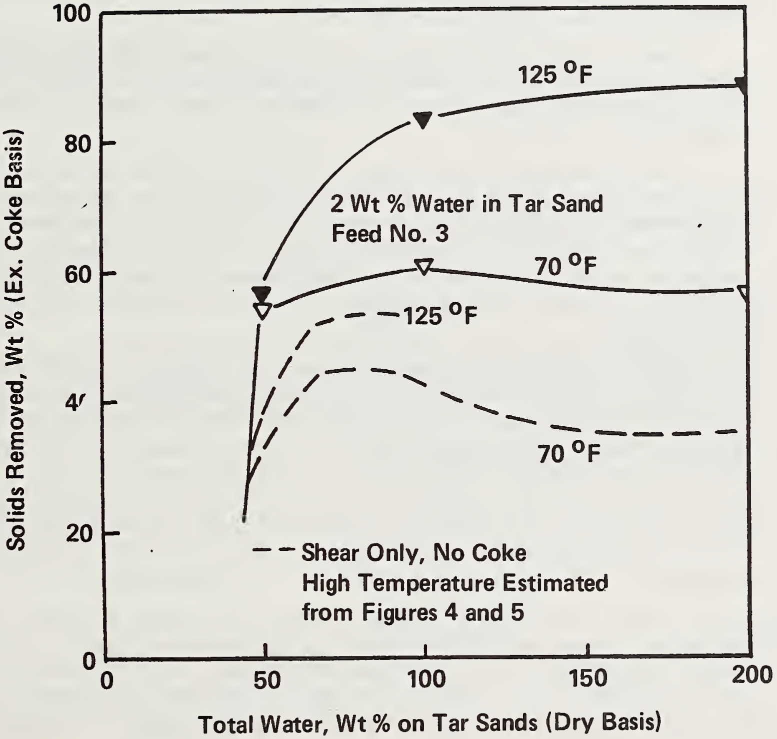


Figure 8-10

Effect of Fluid Coke Addition and Temperature on Sand Reduction with a Low Water Content Tar Sand 25 Wt % Fluid Coke Addition: 5 Minutes Mixing: 100 % Oil Recovery



can result in more consistent results from the different tar sand grades encountered, as will be illustrated later in Section 8-4. The potential improvements of chemical treatment were only briefly explored due to their higher cost, but chemicals play a viable role in the commercial processing of poorer grades of oils sands.

8-2 Agglomerate Separation

Mechanical and flotation techniques of separation were evaluated in small continuous pilot equipment. Mixing was effected using a pug mill.

8-2-1 Mechanical

(a) Submerged Screening

The technique of screening sand from agglomerates under water is most remarkable and has proved to be surprisingly effective for demonstrating the process and evaluating process variables on a continuous pilot plant scale. It has been found that provided the temperature is low, i.e. less than 70°F, then very little or no fouling of the screen occurs provided that care is first taken to clean the screen and make it water wet. The laboratory procedure adopted was to clean with: (1) toluene; (2) acetone; (3) hot soapy water; and (4) cold water.

In bench studies, the largest amount to pass through a 2 square feet of rotary screen in 1 hour without fouling was 210 pounds. However, only a few square inches of this larger screen was being used. A horizontal screen was therefore evaluated as potentially more efficient for larger scale separations.

The screen size chosen was 20 US mesh, to enable most of the sand to pass readily through, and to minimize oil loss to the sand. This is not critical, as data obtained on screen size and shape showed that changing mesh size from 14 to 40 and the slope of the screen from 1 in 6 to 1 in 12 did not change the results significantly, Table 8-5. Larger sized sand that is separated in the agglomerate is still water wet and can be readily removed in solvent dilution clean up of the agglomerate, see Section 9. However, there is an optimum screen size to maximize oil recovery and throughput.

Hence, a pug mill-stationary inclined screen was evaluated and the results of these tests are summarized in Table 8-6. As the runs proceeded, agglomerate covered more and more of the surface of the screen and finally, at the end of the tests, little or no sand was able to pass through. The sand reduction figures shown in Table 8-6 represent average operating values for each run. The actual sand reduction at the end of the run would of course be zero. It is interesting to note that the screen was still water wet at the end of the runs, and the agglomerate on its surface could easily be removed with a jet of water. This probably explains the success of the rotary screen in which the agglomerates and sand particles drop freely from the screen during its rotation thus, "unplugging" the water wet screen for further use.

A vibrating screen was also evaluated, Table 8-6. The screen at the end of run, however, was oil wet over a large portion of its surface. The high frequency vibrations probably packed the small oil particles into the screen openings and facilitated oil wetting. However, it maybe possible that a combination of a steeper screen angle, a more gentle screen motion and perhaps with an elliptical path, might improve the performance of a flat screen to reduce size and increase screening efficiency.

A moving screen belt could be the most effective means of separation based on these preliminary findings especially as it continuously provides a new separating surface as well as an opportunity to wash the screen outside of the separation zone.

(b) Moving Belt

Test runs with a pug mill-hydrophobic moving belt to which the agglomerates could stick and be carried away from the sand in a counter current separation were also evaluated in a series of attempts to devise a suitable system.

The chute from the pug mill was positioned at right angles to the belt, see Position A in Figure 8-11. The oil agglomerates were very l and the majority of them washed off the side belt with the sand. The few agglomerates that adhered to the belt were removed with a spatula from

Table 8-5

Evaluation of Screen Shape (Tar Sands No. 11 30 lb/hr Run No.24)

Run No.	Screen (U.S. Mesh)	Slope (Inch/ft of Length)	In Oil Phase Wt% Solids[(1)]	In Oil Phase Wt% Oil Recovery[(2)]
24 A	14	1 1/4[(3)]	69	98
24 B	20	1 1/4[(3)]	66	100
24 C	20	2 1/2[(4)]	65	100
24 D	40	2 1/2[(4)]	66	100

(1) Average of 4 samples during run
(2) Based on ash determinations of composite sand samples
(3) 7 to 9 1/2 inches in diameter rotary conical screen (1 ft long)
(4) 4 1/2 to 9 1/2 inches in diameter rotary conical screen (1 ft long)

Table 8-6

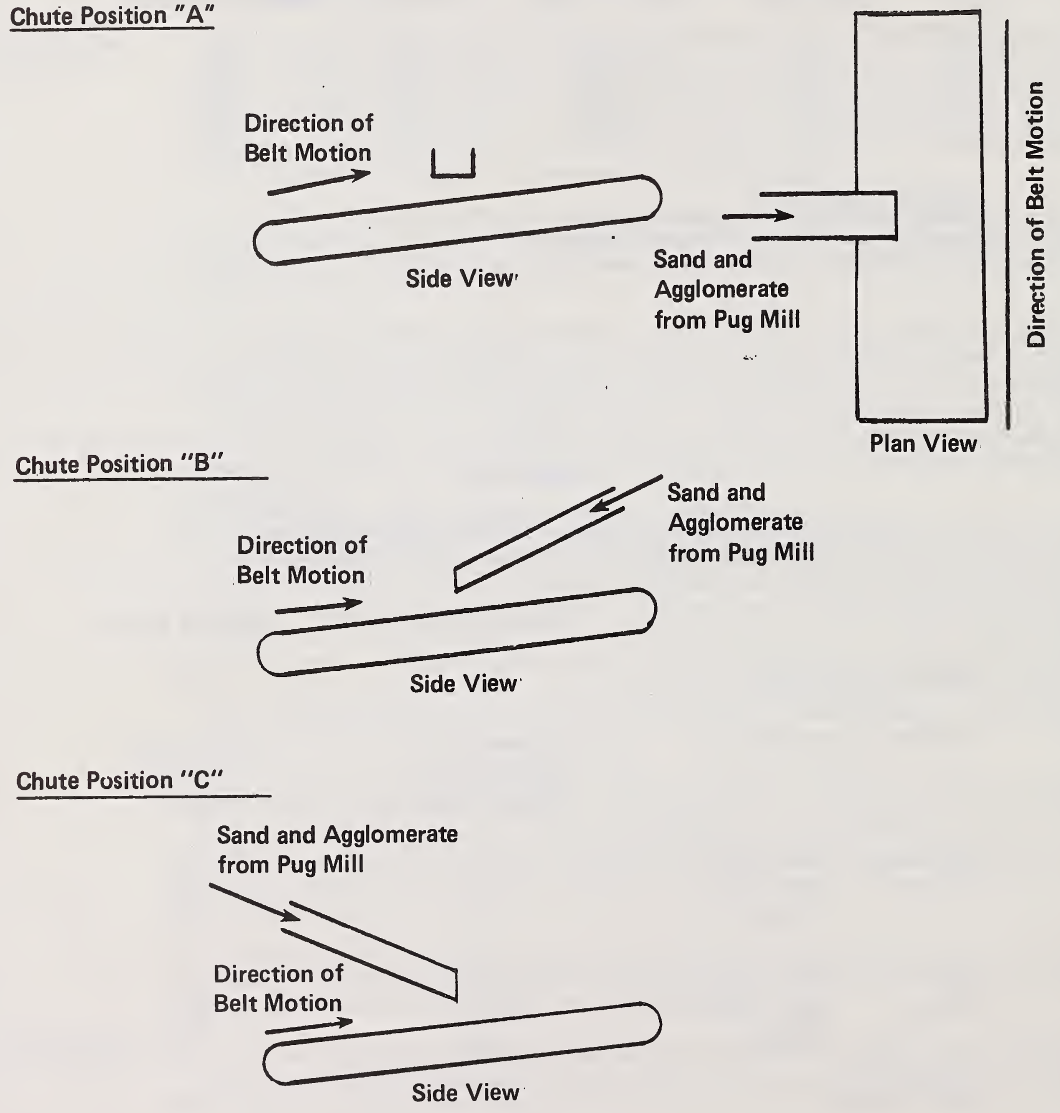
A Flat Inclined Screen is Unsuitable for Separating Agglomerates and Sand (Tar Sand - 19a: Feed Rate - 120 lb/hr : Water/Feed Ratio - 0.75: Screen Area - 1.5 ft2: Screen Slope - 38° to the Horizontal)

		Stationary Screen	Vibrating Screen
Duration of Run - Hours		0.7	1.2
Condition of Screen After Run		Covered with agglomerate - still "water wet"	Covered with agglomerate - "oil wet"
Agglomerate Product	Water - Wt%	17.4	14.6
	Solids - Wt%*	84	72
	Oil - Wt%*	16	28
Sand Product	Water - Wt%	20.8	23.6
	Solids - Wt%*	97.1	99.8
	Oil - Wt%*	2.9	0.2
Solids Reduction		21	60
Oil Recovery		96	99

* Dry Basis

Figure 8-11

Relationship between Pug Mill Chute and Belt for Runs 8-14



the end of the belt. A build-up of sand and oil on the belt rollers increased the tension on the belt and the run had to be terminated after 30 minutes.

The chute was turned parallel to the belt as shown by Position B. The agglomerates were again quite small and tended to roll down the belt with the sand. A layer of sand on the belt directly under the chute prevented the agglomerates from sticking as they fell. A metal knife edge was mounted at the upper end of the belt but could not be moved close enough to its surface (because of the belt lacing) to adequately remove the agglomerate product. The chute was turned through 180° to Position C. A water spray was directed under the chute to keep this area of the belt reasonably free from sand. The oil agglomerates were much larger and readily adhered to the belt. The knife edge finally cut the belt lacing after 30 minutes and the run was terminated.

A number of alterations were made with metal plates installed along the sides of the belt to keep the smaller agglomerates from sliding off the edge before they had a chance to stick. The pug mill chute was returned to Position B. The number of water sprays was increased from two to five and an air jet was added to blow off excess water from the surface of the agglomerate before it reached the end of the belt. The agglomerate was removed manually. An idler roller was installed at the "sand" end of the belt to trap any small oil particles. This run was fairly successful although some free sand was still caught under the agglomerate and large number of small oil particles appeared in the sand product. The agglomerate contained 48.8% oil which compared favourably with the corresponding results from the rotary screen tests. Although, these tar sands had undergone some aging.

A teflon knife edge mounted on a flexible bracket was used for direct contact with the belt without damage to the belt lacing. One additional water spray and a second air spray were installed. The agglomerates were turned over manually once while under the water spray to remove sand trapped beneath. This run demonstrated that continuous operation could be achieved with the only major problem being a somewhat greater loss of oil to the sand than desired.

Oil recoveries ranged from 71 to 98% and solids reduction from 82 to 87%. Part of the agglomerate was returned through the water sprays a second time, but only small gains in solids reduction were achieved.

In the final two tests in this series, the idler roller at the "sand" end of the belt was replaced by a power-driven brass roller. The latter had a number of grooves cut in its surface which were intended to permit the sand and water to pass through but not the oil particles. A groove depth of 3/32" was initially chosen, but this proved to be too shallow to pass the sand-water slurry at the required rate. The sand product, however, was oil free. The groove depth was increased to 1/4" and a one-hour test was carried out.

Agglomeration was not fully developed at the start of the run, and many of the smaller oil particles passed through the grooved roller. However, as the run proceeded, the number of these small particles decreased considerably, and at the end of the test, the sand was essentially oil free. The oil recovery increased from an initial value of 89% to 99+%. Solids reductions averaged 78% for agglomerate passed once through the water sprays. This was increased to 83% with a second pass to wash the agglomerates.

The conveyor belt concept could be made to give solids reduction and oil recovery results equivalent to those obtained with the rotary screen, provided agglomeration is well developed. The former is more effective in removing gravel but less effective for sand. A better washing technique could be devised for the belt conveyor than was used in these experiments that would give better and more consistent results.

It was concluded that a submerged screen in the form of a moving belt that could be cleaned during operation was the best mechanical mode of separation. Conveyor belt washing of aglormerate appeared to be a good method of removing gravel.

8-2-2 Flotation

a) Reduced Pressure

(i) Glassware Experiments

Some of the very small amount of gases in the tar sand structure are dissolved in the oil. Thus, reducing the pressure above a mixture of tar sands in water releases these dissolved gases, that form adhering bubbles and float the oil phase as a cohesive froth.

A typical relationship of the relative volume of the oil phase with associated gas at reduced pressures and at different temperatures is shown in Figure 8-12. The data was obtained by measuring the relative change in volume of small portions of an oil phase in a graduated tube, immersed in a temperature bath, and connected to a system controlling the reduced pressure at any desired level. The lower limit of reduced pressure at a given temperature is governed by the boiling point of water. The upper limit of pressure for the oil phase to float is governed, approximately, by the apparent density. The density of the oil phase (agglomerate) used in these study, were approx. 1.7 g/ml at 70°F.

The relationship of reduced pressure and temperature at which the same oil phase floated in water is shown in Figure 8-13. The same experimental technique was used to obtain these data, except the oil phase was initially submerged in water. The area under the curve and above the vapour pressure of water represents conditions at which flotation operations could be carried out.

The general patterns illustrated in Figures 8-12 and 8-13 apply only to the specific oil phases used. Variations in gas and solid contents of the oil phase would displace the parameters. The lower the solids content or greater the gas content, then the higher the pressure will be at which flotation will occur. As mixing tar sands with water at higher temperatures effects separation of larger amounts of solids, and the lower the solids content of the oil phase then the higher the pressure required to cause flotation at high temperatures, then the hot water separation process at atmospheric pressure is represented by the point on the upper pressure limit in Figure 8-13. The dissolved hydrocarbon gases in the oil play a very useful role in decreasing the apparent density of the oil froth in this process. However, not all the oil in the tar sand is associated with adequate gas for flotation at high temperature, so that additional air is added in slurrying with water under alkaline conditions, that is crucial for achieving good oil recoveries.

However, reduced pressure at lower temperatures is a substitute for high temperature flotation that is transposed for commercial operation Sections 6 and 7. The application of reduced pressure to separation is illustrated by the following experiment, in which a 100 g sample (dry basis) of tar sands No. 24 containing 7 wt% connate water and 13 wt% oil was mixed using a mortar and pestle with 30 wt% water for half a minute to effect disintegration of the tar sands into sand and very small oil particles distributed in water. This was carried out at 45°F. The mixture was transferred to a flask containing excess water (approx. 170 wt% on tar sands) and the pressure was reduced. When the pressure reached 200 mm Hg, some oil floated to the surface. At lower pressures, increasing amounts of oil floated to the surface. In less than half a minute from starting the evacuation, separation was complete at about 80 mm Hg with sand remaining at the bottom of the vessel. However, the pressure was reduced further down to about 20 mm of Hg without any further benefit.

It was observed that the very small oil particles that floated to the water surface immediately coalesced, forming a large cohesive agglomerate. This large oil agglomerate was skimmed off the surface of the water. The sand contained some oil particles that did not float; presumably these oil particles contained solids and little or no gas, although occlusion of air in more appropriate mixing could reduce losses. The solids removed, as wt% of total solids in the original tar sands was calculated to be 80%; and the oil recovery in the agglomerate was about 80 wt%.

It should be noted that a minimum of mixing was used to breakdown the tar sand structure. It has also been found that complete recovery of an oil phase can be obtained by mixing with water to effect agglomeration and separating the agglomerates by reduced pressure flotation.

Figure 8-12

Apparent Oil Phase and Associated Gas Volume Changes with Temperature and Pressure (Oil Phase Contained 74 Wt % Solids)

FIGURE 8–12

APPARENT OIL PHASE AND ASSOCIATED GAS VOLUME CHANGES WITH TEMPERATURE AND PRESSURE

(Oil Phase Contained 74 Wt % Solids)

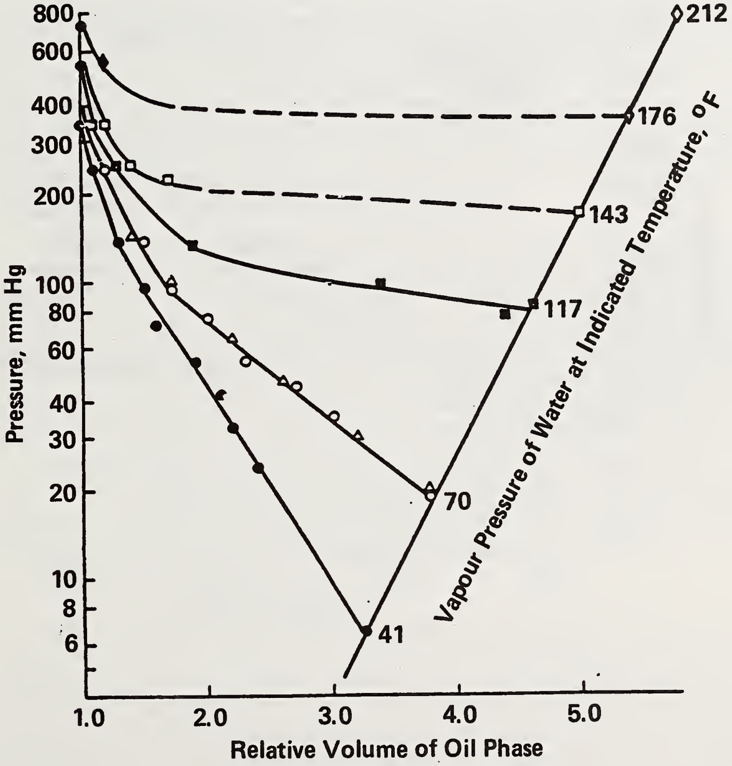
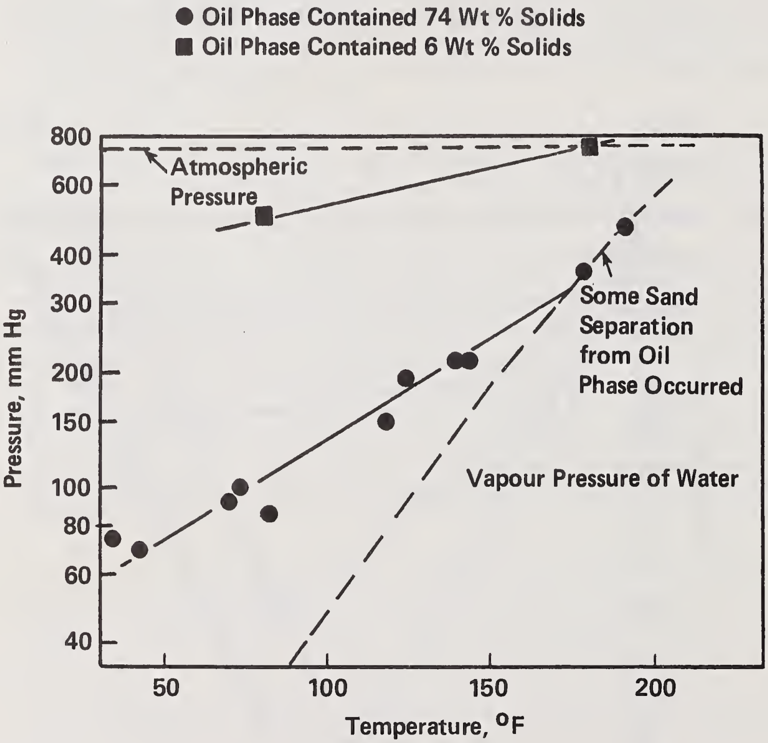


Figure 8-13

Temperature and Pressure Relation at which Oil-Phase Flotated on Water (Points Are Average of 2-6 Measurements)



This is illustrated by the following experiment. A 100 g sample (dry basis) of tar sand No. 4 containing 5 wt% connate water and 15 wt% oil was mixed with 70 wt% total water using a mortar and pestle (this is about an optimum amount of water as discussed before) for three minutes to effect agglomeration. The mixture was added to 100 wt% of water in a flask and subjected to a vacuum. At about 200 mm of mercury pressure, oil appeared at the surface and the separation was very rapid at lower pressures. The total time to accomplish complete separation of the oil phase was less than one minute from the start of evacuation.

When the separation was complete, 66 wt% of the total solids was recovered as clean oil-free sand from the bottom of the vessel. This "Sand Reduction" value is the same as that obtained by mixing with water and mechanical separation; i.e. sieving with this particular tar sands that had undergone some aging, Figure 8-14.

(ii) Bench Equipment

Two methods of separation were devised on a larger scale. The equipment used is illustrated in Figure 8-15. Actual pressures in mm Hg used were approximately twice the vapour pressure of water in experiments in which oil recovery and sand reduction were measured.

In Method A, a simulated continuous demonstration with the pug mill used in the batch operations and a glass separator was attempted. Disengagement of the oil from the sand in feeding and the pressure due to the height of material between the feed point and the overflow were problems. An improved approach to the separation based on this operation, would utilize the feed introduction either at the oil-water interface or just above or just below, and a minimum distance between the interface and the oil product overflow. A feed distributing system would also appear to be advantageous. It is envisaged that a commercial operation using this type of reduced pressure flotation separation, besides incorporating these improvements in the design, would use barometric legs to withdraw the product streams.

In Method B, the mixing action of the paddles was utilized to aerate and to help raise the oil phase to the surface of the mixture and effect its disengagement as a froth. In the experimental technique, most of the oil product was readily collected and sampled by rapidly breaking the vacuum and skimming the froth, that only sank very slowly due to gas loss and surface effects. In a commercial operation, separation of the oil phase could be achieved by skimming the froth from the surface of the mixer and pumping out the froth and/or withdrawing the product streams through barometric legs. This not only combines mixing and separation functions, but results in high unit capacity due to the rapidity with which separation occurs under reduced pressure.

The results of these bench operation are summarized in Table 8-7. The same conclusions may be drawn as those from the i.e. glassware operations that; (a) better oil recoveries are obtained with longer mixing time to effect agglomeration; and (b) reduced pressure flotation and submerged screening give essentially equivalent results.

(iii) Additional Vacuum Separation Studies

It has been shown that a critical temperature pressure relationship exists that determines whether an oil particle will float or sink in water, and hence the solids content is an important parameter. For example, at 100°F' a particle containing 6 wt% solids will float at pressures below 500 mm Hg. However, when the solids content is increased to 74 wt%, the pressure must be reduced to less than 100 mm to effect flotation. Further, experiments described above showed that roughly 80% of the solids could be removed by mixing the tar sand with 70°F water and applying a vacuum to effect flotation. The oil recoveries ranged from 80 to 100%.

Forty grams of tar sands were mixed for two minutes with 30 grams of water in a mortar and pestle. The resulting pulp was transferred to the right-hand leg of a glass apparatus in the shape of an h. Both legs were filled with water and the high speed vibrator in the right-hand leg adjusted to fluidize the slurry. The temperatures of the initial water used in mixing, the "flooding" water, and the water in the surrounding temperature control jacket were all adjusted to a pre-determined value. After one minute of vibration, vacuum was applied through a line at the top of the left-hand leg. An oil froth collected in the neck of the apparatus. It was expected that on releasing the vacuum, the froth would collapse and fall to the bottom of the left-hand leg. In

Figure 8-14

Flotation of Agglomerates

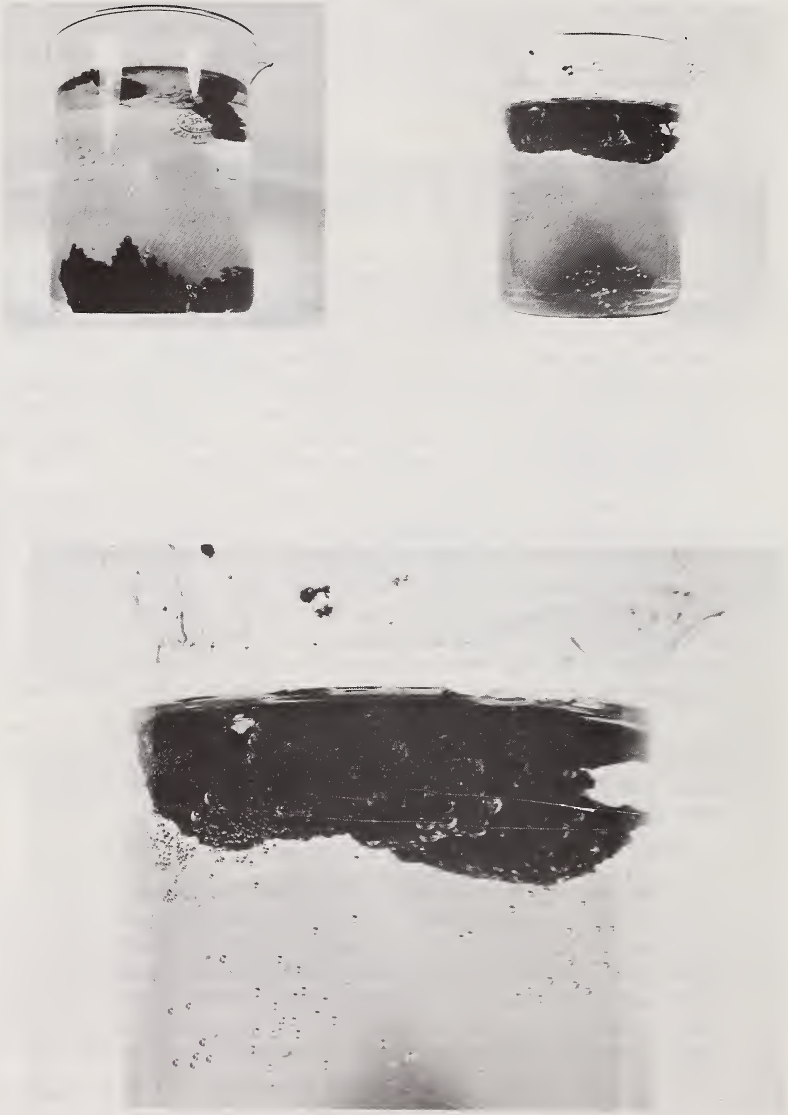


Figure 8-15

Techniques of Separation Using Reduced Pressure

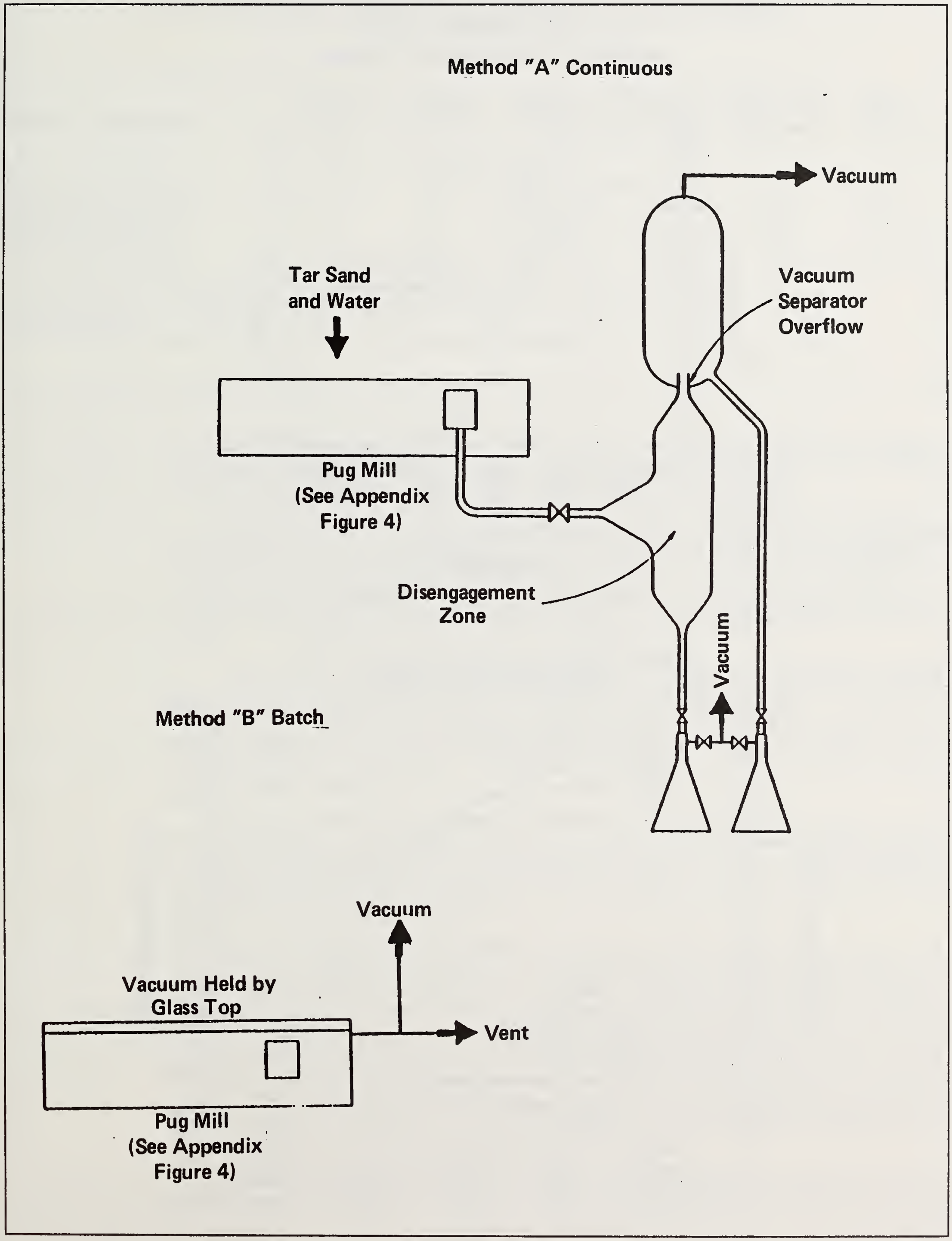


Figure 8-16

Oil Recovery from Area B Tar Sand

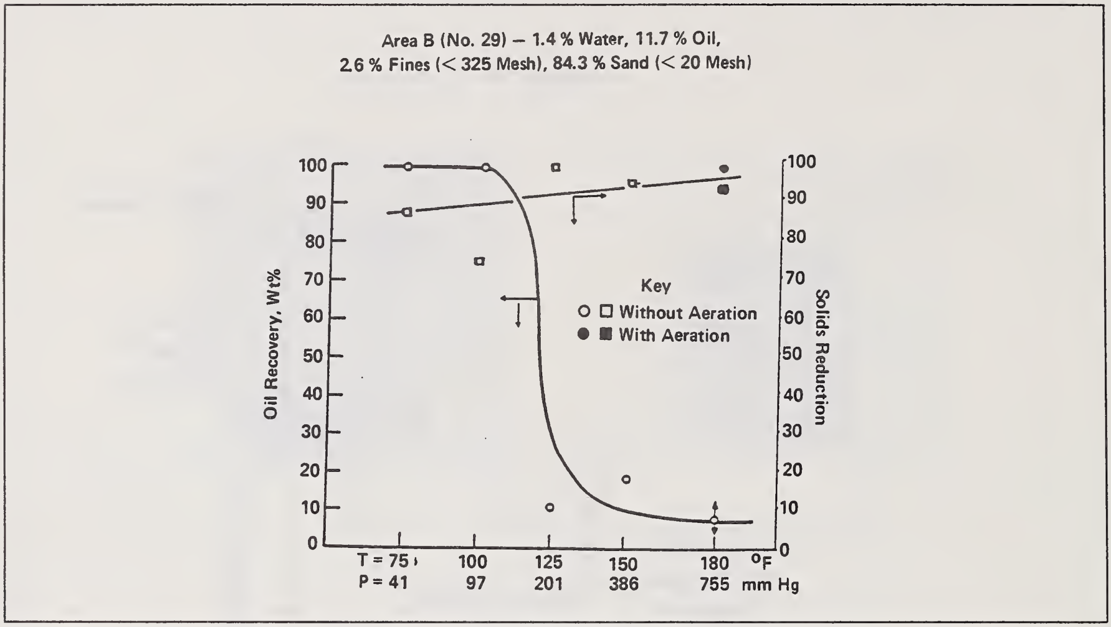


Figure 8-17

Oil Recovery from Area D Tar Sand

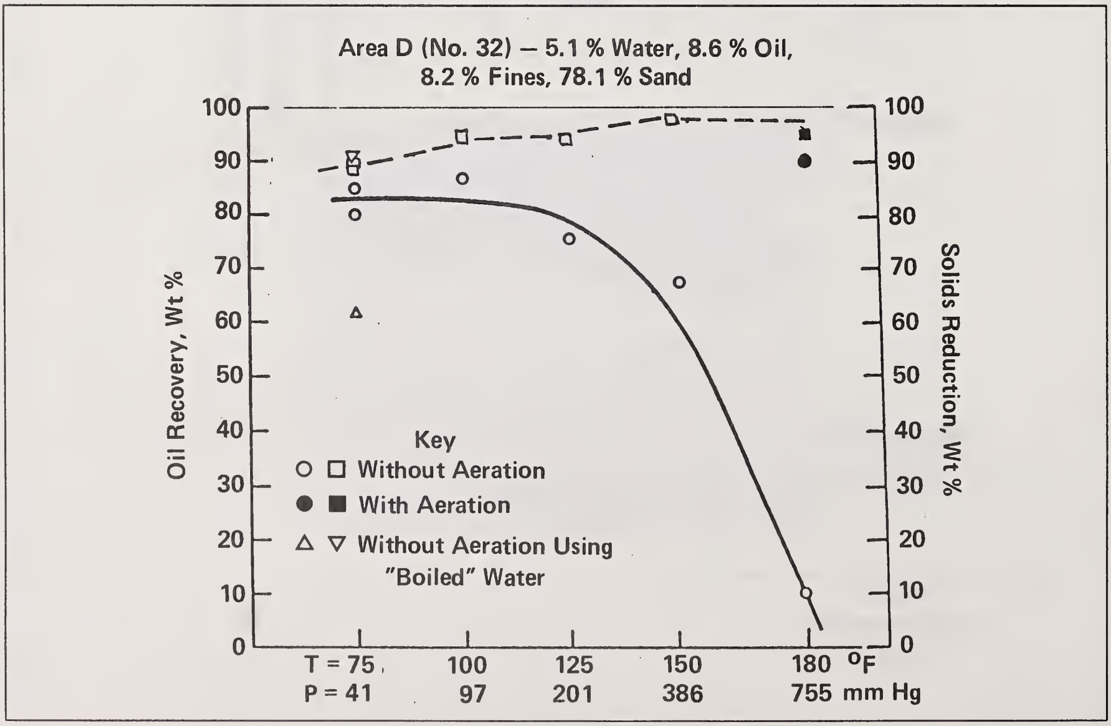


Table 8-7

Comparison of Separations Using Reduced Pressure Flotation and Submerged Screening (Mixed with 75 Wt % Water on Tar Sands (Dry Basis) at Room Temperature 70°F)

Method of Separation	Tar Sand Number	Mixing Time, Min	Pressure mm Hg	Wt% Oil in Oil Phase	Wt% Solids Removed	Wt% Oil Recovery
Reduced Pressure(1)	8	1.0	50-200	45	79	92 (Est)
Submerged Screening(2)	8	5.0	Atmospheric	32	63	100
Reduced Pressure(3)	11	5.0	50-200	60	88	100
Submerged Screening(2)	11	5.0	Atmospheric	60	88	100

(1) Apparatus used was a pug mill fitted with a glass top and operated under reduced pressure, 100 mm Hg, Method B.
(2) Mortar and pestle.
(3) Tar sand was mixed in a pug mill and the mixture was separated in the glass apparatus, Method A.

all cases, however, the froth remained in the neck of the vessel and was removed with a spatula. The main portion of the solids remained in the right-hand leg; in a few cases, there was some carry-over of mineral matter into the left-hand vessel due to excessive mixing.

Evaluation of the effect of pressure temperature conditions on flotation were obtained for a good Area B and a poorer Area D grade of oil sands, Figures 8-16 and 8-17. The oil contents of the two "products" (i.e. froth and solids) were determined by ashing. The mineral matter in the froth was assumed to be clay with an ash of 92.0 wt%. The mineral matter in the solids was assumed to be sand with an ash of 99.7%. Oil recoveries and solids reduction values were calculated.

In this series of experiments the various conditions of temperatures and pressures, ranging from room temperature and high vacuum to 180°F and 1 atmosphere. There was no method of calculating the pressure which should be used for a particular temperature. Hence, the pressure was taken arbitrarily at the same fraction above the vapour pressure of water (roughly twice) as that used in the hot water process. A minimum limit in each case would be the vapour pressure of water at that temperature.

It has been shown that the difference in densities between water and oil changes very little in the temperature range 100-200°F. Therefore, the change in density of the oil flecks must be due to the competing effects of the mineral and gaseous components. The gas laws would permit an estimation of the effect of temperature on the occluded gas bubbles if their initial volume were known, that is an unrealistic case.

The oil recovery results were highest at low temperatures and high vacuum (Figures 8-16 and 8-17). The most remarkable feature was the extremely poor recovery (roughly 10%) obtained with the "hot water" conditions; i.e. 180°F and 1 atmosphere. To see if the discrepancy was due to the lack of air for "flotation", a hollow rod was used for the vibration shaft through which was passed a slow stream of bubbles. The oil recovery increased to well over 90% for both tar sands, in agreement with the values usually obtained in the hot water process. It would be a safe assumption that high recoveries could be obtained for all the pressure-temperatures combinations if some suitable aeration was employed. This is an extremely important observation for not only the operation of the hot water flotation process by occluding air slurrying, but for the development of a cold water flotation separation process.

The solids reduction and oil recovery values at the high temperature-atmospheric pressure conditions are slightly higher that is probably due to superior mixing and shearing at the elevated temperatures. The Area B tar sand tended to form large agglomerates at low temperatures that float before all the water-wet solids were released. These results at low temperature-high vacuum ,conditions (without external aeration) might be due to the formation of air bubbles during evacuation. The drop in recovery (80+% to 61%) when boiled water was used, Figure 8-17, tends to support that this effect was at least partially responsible.

It was concluded that a low temperature, reduced pressure, separation process is technically feasible. Some air addition at an appropriate location in the system would be used to assist flotation. Although, air addition would be a serious debit for a vacuum process and might possibly cancel out some of the economic advantage from low temperature over the hot water process. The cold water froth quality is not as good as that obtained with the conventional hot water process, but perhaps could be improved with more severe mixing prior to and during reduced pressure separation, i.e., a combo process. Chemical assisted flotation is another approach.

(b) Hydrocarbon Gas Flotation

Flotation of the oil on water at high temperatures, either in the hot water separation process, or in a reduced pressure separation process have been described above. The importance of the connate gas dissolved in the oil to these methods of separation has also been pointed out. An extension of these methods would be to mix tar sands with hydrocarbon gases under pressure to increase the gas content of the oil and then with water, so that on release of the pressure, the oil floats at atmospheric conditions.

A preliminary experiment using this type of operation was carried out in which a 450 g sample of tar sands was mixed at room temperature for 5 minutes under pressure, maintained at 10 psig. Water, 690 g, was introduced and mixing continued for 5 minutes. The pressure was then released and oil as a froth floated to the surface of the water and was skimmed off. The remaining oil phase-sand-water was screened, as in previous sand reduction experiments, to recover sand, clay and a second oil phase. The results of this experiment are summarized below:

HYDROCARBON GAS FLOTATION PROCESS

Product	**wt% on Tar Sands** (dry basis)	**Wt% Oil in Product** (dry basis)
Floatable Agglomerate	33	44
Non Floatable Agglomerate (Screened)	12	35
Sand and Clay Reduction	55	1

These preliminary results show that this method of separation is possible, but further work is required to define the variables of this approach to give complete oil recoveries in the froth. However, the success of these initial experiments tend to support the proposed role of connate gas in the oil sands as a contributing factor in flotation.

(c) Denser Media Flotation

Separation by "oil flotation" may also be achieved by difference in density created by the presence of solids in the water phase; e.g. fluidized sand bed and/or clay suspension in water. The idea to use a fluidized solids bed to create a denser medium than oil to effect separation by flotation was tried, Figure 8-18. In these preliminary operations, water was used to fluidize the sand bed. Entrained air in the water appeared to be a factor. The use of recycled clay-water mixture may prove useful in increasing the density of the bed. A key mechanism of agglomerate loss into the sand bed appeared to be due to water injection creating channels down, which small agglomerates are dragged in hydrodynamic flow pattern. Simultaneous introduction of air with water resulted in the small agglomerates being dragged back to the upper agglomerate phase that is more distinctly separated by the aeration. This continuous separation technique can only make a rough cut and further investigation and scale-up is needed before considering this approach as a feasible alternate method of separation.

(i) Comparison of Methods

A preliminary comparison of the methods described above are shown in Table 8-8 and 8-9. It can be seen that essentially equivalent results were obtained with each method. However, further investigation and scale-up development of these methods are required before a realistic

Figure 8-18

Separation by Fluidized Solids Flotation

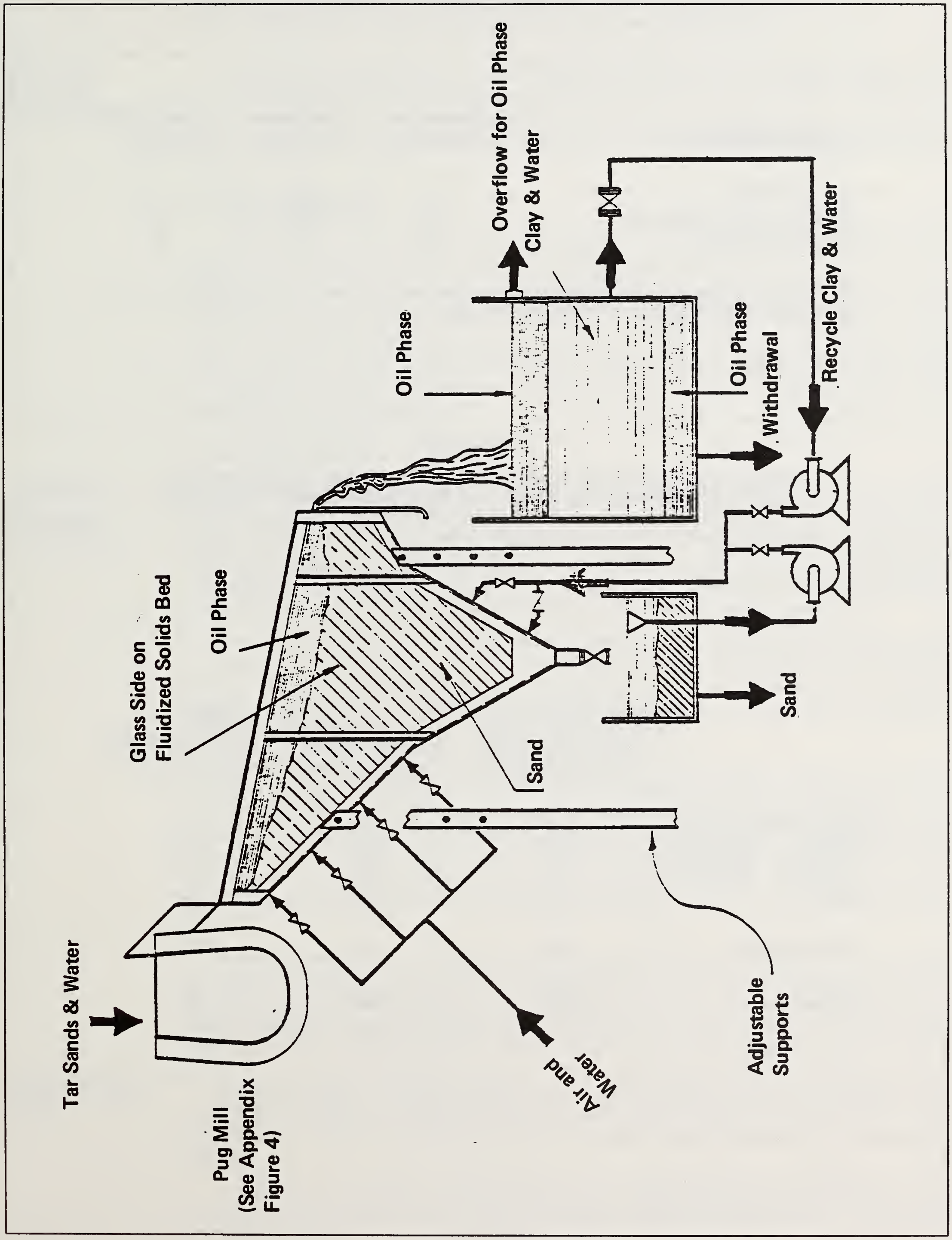


Table 8-8

Preliminary Comparison of Continuous Methods of Separation (Tar Sand No. 11 ; 70°F)

Method of Separation	Submerged Screening	Fluidized Solid Bed	Reduced Pressure
Oil in Oil Phase	60	55(1)	60
Oil Recovered in Oil Phase	100	99	100
Sand Reduction Wt%	88	85	88

(1) Average of: 20% oil phase containing 79.5% oil that floated on water (aerated?), and 80% oil phase containing 49.5% oil that was heavier than water and included some overflowed water wet solids.

Table 8-9

Belt Conveyor and Rotary Screen Are Equally Effective for Separating Agglomerates and Solids (Tar Sand - 19a: Feed Rate - 60 lb/hr: Water/Feed Ratio - 0.75 W/W)

		Using Rotary Screen	-------------Using Belt Conveyor-------------	
		Good Agglomeration (Av - Runs 1 and 2A)	Fair Agglomeration (Start of Run 14)	Good Agglomeration (End of Run 14)
Agglomerate	Wt% Clay	8.5	8.4	7.7
Analysis	Wt% Sand	31.3	50.0	44.0
(Dry Basis)	Wt% Gravel	14.8	2.0	1.9
Wt% Oil		45.4	39.6	46.4
Solids Reduction		81.2	78	83
Oil Recovery		99.2	89	99+

quantitative comparison can be made. This comparison should be made for several different types of oil sands that will most probably be encountered in a commercial operation, although preliminary evaluations on the effects of bitumen recycle and chemical additions indicate that similar results can be obtained with lower grades i.e. 6% as higher grades.

8-3 Continuous Processing

A continuous demonstration of Sand Reduction was first carried out using a single screw mixer and a submerged rotary screen. Subsequent demonstrations used either ribbon mixing elements, intermeshing screws, or combination pug mill that is a scaled down version of a type of mixer used in the minerals industry, with a submerged rotary screen as a convenient separation technique.

8-3-1 Mixer Designs

A series of experiments was carried out to evaluate the type of mixing action required in sand reduction. The types of batch mixers that were studied are summarized in Table 8-10. In general, the results are very similar with the exception of oil recovery. On this basis of comparison, the mixers formed two groups that gave: (1) poor agglomeration; and (2) good agglomeration. It appeared that a square helix essentially duplicated the action of the mortar and pestle, and that a kneading action, such as obtained in a dough kneader or pug mill, gave good results. Also, it was observed that the mixer parts tended to become covered with a layer of oil. This appeared to both aid agglomeration, as well as protect the equipment from the abrasive action of the separated clean sand.

8-3-2 Demonstrations

(a) Helix and Submerged Rotary Screen

This original unit was built to demonstrate the sand reduction process on a continuous basis. A flow diagram is shown in Figure 8-19. In this equipment, tar sands and water were fed to a hopper and in turn, to a helix mixing element, that had been found to simulate the mortar and pestle operation. Provision was made to vary the temperature of mixing. The mixture passed into a submerged rotating screen, that separated the sand from the agglomerate. The product streams were withdrawn through valves. The agglomerate, however, was heated to facilitate flow.

It was found that an oil scum sometimes collected slowly on the surface of the water, above the screen. The amount of oil varied with the tar sand feed. Estimates indicate this oil to be from 0 to 2% of the total oil in the feed. However, provision was made to recover this oil by overflow, settling and recycle of water. The size and shape of the screen could be changed, and a ribbon mixing element was also made interchangeable with the solid helix.

A comparison of some runs carried out on this unit are summarized in Table 8-11. It can be seen from the first two comparisons in this table that tar sand feed quality is an important variable. The sand reductions obtained in this unit with fresh and old tar sand agreed with those obtained in a mortar with a pestle, as illustrated in Figure 8-10. This suggests that this aging effect is not due solely to loss of water, but may involve some other structural change, perhaps caused by the spreading of oil at gas-water interfaces in the structure at ambient temperatures. However, the best sand reduction results were obtained with fresh tar sands of relatively high connate water.

The third comparison in Table 8-11 shows the solid helix to be superior to the ribbon, whereas, it was observed previously, in the batch operations, that these two elements were about the same. The capacity of the solid screw at less than 50 lb/hr, however, was lower than the helix and not suitable for scale up. Feeding from the hopper into the small intake to the screw was sometimes difficult, so that larger multi screw units were considered more practical for scale up.

(b) Intermeshing Screw

Earlier pilot plant experiments using a single screw, Figure 8-20 for mixing and a submerged rotary screen for separating, gave reasonably good sand reductions of ~88%. The capacity of the screw, however, was fairly low at less than 50 lb/hr and feeding was sometimes difficult.

A small unit was therefore constructed that had two intermeshing screws, Figure 8-20, to see if a high shear-high capacity mixer could be developed. Although the screws were very short, the

Table 8-10

Mechanical Batch Mixing Operations (Tar Sand No. 8 Range of Conditions: 3-8 Minutes Mixing; 65-140 Wt % Total Water; 70°F Temperature. Product Screened from Sand Using 20 Mesh Sieve in an ASTM Shaker)

------------------------------Mixers That Gave Poor Agglomeration--------------------------------

Mixer	Results (Wt%)	
Grease Mixer	Solids Removed	61-68
"Hobart" Mixer	Oil in Oil Phase	26-39
"Hobart" Beater	Water in Oil Phase	12-13
Tumbler	Oil Rec. in Oil Phase	75-92

------------------------------Mixers That Gave Good Agglomeration------------------------------

Mixer	Results (Wt%)	
Pestle and Mortar	Solids Removed	59-69
"Full View" Mixer	Oil in Oil Phase	30-36
(a) Square Helix	Water in Oil Phase	14-20
(b) Ribbon	Oil Rec. in Oil Phase	94-100
Kneader		
Pug Mill		

Table 8-11

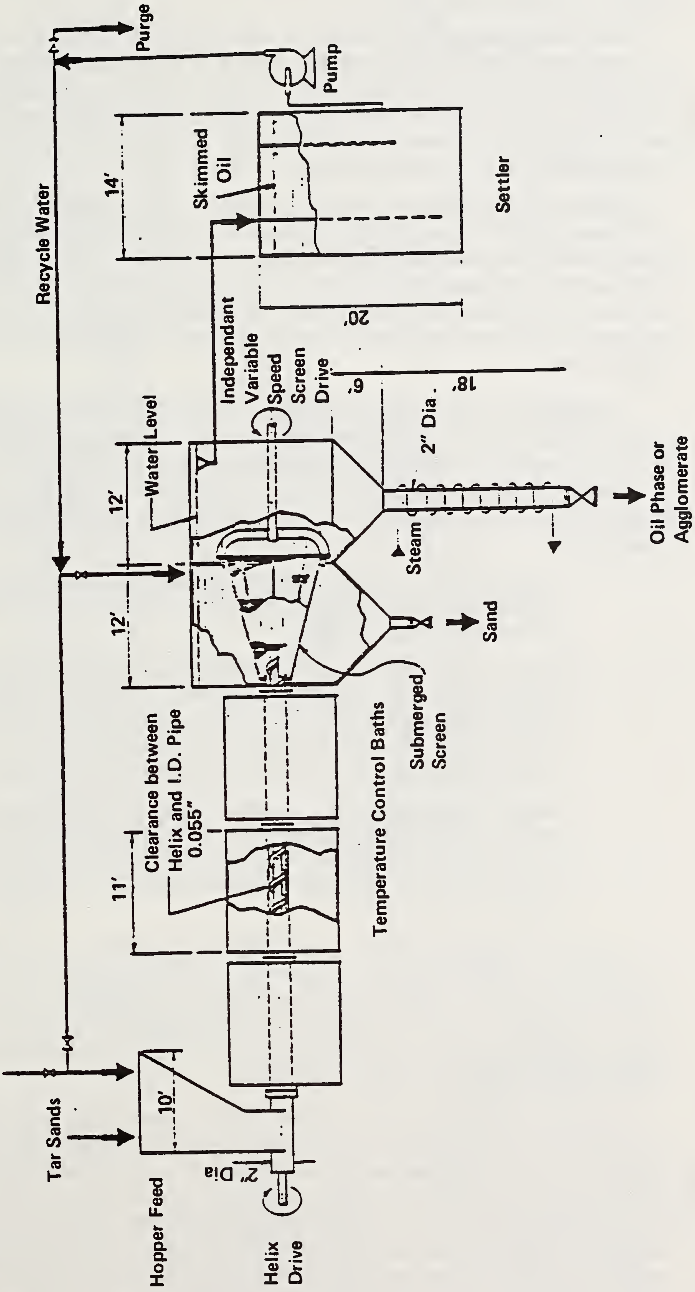
Sand Reduction Experiments with Continuous Screw (Feed Rate : 30 lb/hr Tar Sands and 25 lb/hr of Water)

Tar Sand Sample			Temp. °F	Wt% Solids Removed	Wt% Oil in Agglomerate(1)
Number	(% Water)	Type			
---------- Effect of - Feed Quality ----------					
8	5	Old	70	62 (63)(3)	32
9	5	Fresh	70	83 (81)(3)	45
11	6	Fresh	70	88 (88)(3)	60
---------- Effect of Aging(2) (or variations in feed) ----------					
11	6	Fresh	70	88	60
11	6	Fresh	70	79	44
11	6	Fresh	60	73	38
---------- Effect of Mixing Element ----------					
Solid	6	Fresh	70	88	60
Helix: 11	6	Fresh	70	81	48
Ribbon: 11					

(1) Dry Basis
(2) Runs from April 20 to May 10
(3) Mortar and pestle results in parenthesis

Figure 8-19

Continuous Screw and Rotary Screen



sand reduction and oil recovery for Area B tar sands were surprisingly good, the former varying from 63 to 76% and the latter from 93 to 99%. With Area D feeds, however, agglomeration did not occur. It was found that by applying pressure to the feed hopper with a wooden plug, it was possible to maintain a uniform feed rate of 40 lb/hr. Pumping capacities at critical slurry composition were many times larger.

Brief demonstrations were carried out with this screw apparatus mounted vertically. Feed and water were introduced at the centre, clean sand settled to the bottom and agglomerate was removed from the top. This showed that it may be possible to agglomerate and separate in a single unit. Other variations were conceived, but not developed, such as four intermeshing screws set in a square pattern of alternating left and right-hand screws for evaluating counter current separation of sand and agglomerate.

Based on these preliminary equipment studies, a larger intermeshing screw was constructed of the same size as the pug mill used in most of our other demonstrations of the process. This high capacity unit was capable of processing over a tone/day of oil sands. Sand Reduction performances with the intermeshing screw was significantly better than with the pug mill. This was attributed to the higher shear achievable in this type of mixer, that was particularly effective in processing 50/50 blends of Areas D (poorer)/B (good) oil sands compared to only 25/75 blends in the pug mill.

(c) Pug Mill

A design of a typical pug mill mixer, that was commercially available and used in the mineral dressing industry, was scaled down for use in these small demonstrations of the Sand Reduction process. This type of mixer is illustrated in Figure 8-18, and was used together with an inclined submerged screen not only to demonstrate the process at Sarnia and on-site at Mildred Lake, but to evaluate the effects of design and process variables. Operating effects found were:

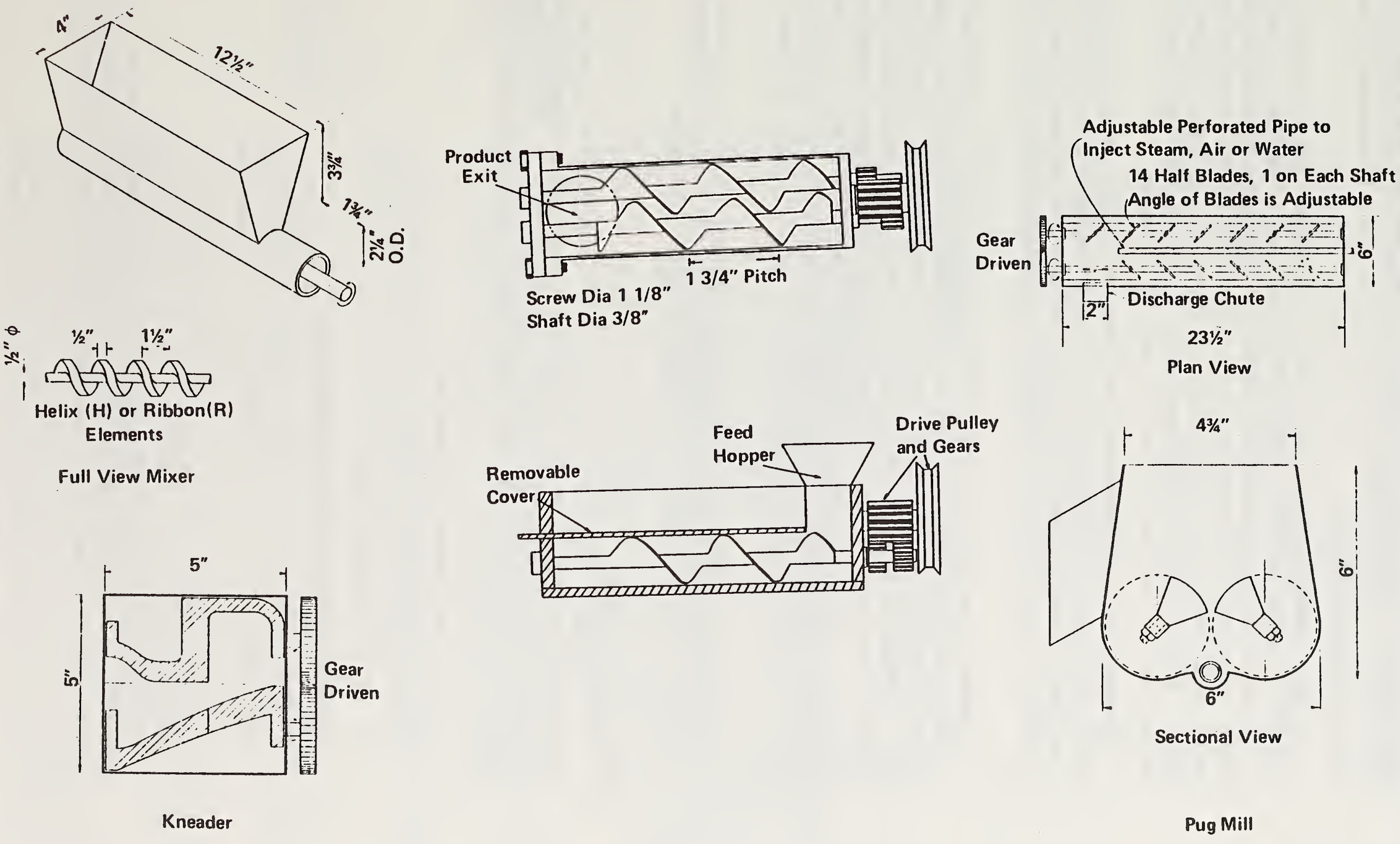
- *-high water rates produced larger agglomerates and freed occluded sand, but the agglomerates contained more sand due to the lower shear needed to breakup the agglomerates to release solids.*
- *-high weir (overflow) height was needed at the beginning of the test until some degree of agglomeration had been established, then the weir height was lowered in increments over a 30 minute period. Thus, a suitable low weir level was obtained and maintained in the pug mill enabling the discharge of large agllomerates without creating a dead zone at the bottom of the pug mill for sand and gravel.*
- *-quarter circle paddles at 45° forward gave a positive feeding action at highest throughput, but larger agglomerates were obtained at 90° presumably due to the longer residence time of the oil particles in the pug mill. Full disc paddles are superior to the quarter disc paddles as the slurry ingredients are forced to travel in a longer tortuous flow.*

In general, good quality Area B oil sand separated easily in a pug mill, resulting in good sand reduction (~ 88%) and high oil recoveries of (~ 98%) in large oil agglomerates, as much as 1-2 inches in diameter. Similar results were obtained with marginal quality Area B oil sands, except smaller agglomerates were attained by suitably adjusting the pug mill operation. Thus the pug mill could be made to essentially match the superior result of the intermeshing screw with this feed using this type of tar sand, Table 8-12.

Pug mill tests at ambient temperature of 70°F indicated that blends containing 25% or less of Area D with good quality Area B oil sands, could be processed with essentially the same results as Area B. The intermeshing screw, however, was more successful in processing blends with oil recovery of 99% from blends within 25% of Area D, and 90-95% with blends of 50% area D. Visual appearance of the agglomerates leaving the screw indicated that 50% of Area D was close to the maximum level that could be processed without losing agglomeration. The superior performance of the intermeshing screw over the pug mill was attributed to the generation of higher shear in the slurry with the 0.75 critical ratio of water to tar sands.

Figure 8-20

"Good" Mixers for Agglomeration



8-4 Comparison with Hot Water Separation

The experimental small scale continuous pug mill and intermeshing screw with inclined submerged rotary screens were also evaluated at Mildred Lake on marginal quality oil sand samples taken from the feed to the CSA pilot plant. Although these marginal oil sands represent only a small, but significant part of the CSA site, they will have to be eventually processed as part of a commercial operation.

The basic approach in Sand Reduction pilot unit development plan was to simply engineer the process at ambient conditions. Although this is quite feasible with Area B tar sand, Table 8-12, that represents the larger portion of the deposit, this was less than successful on Area D marginal oil sands, that had undergone some reworking. Initial comparisons with Hot Water Flotation on essential the same tar sands, resulted in oil recoveries for Sand Reduction that were higher by 5-10%. However, oil agglomeration was not optimized for product quality from the marginal feeds used, and sand reductions were only 80% of expected.

Subsequent laboratory evaluations of these same tar sands showed that better and superior product qualities were possible from Sand Reduction with marginal oil sands, when conditions were optimized and agglomerate (oil) recycle was used to seed the process, together with chemical treatment to counteract any tar sand aging effect that may have taken place, see Section 8-5-2.

In summary, Sand Reduction has a 5-10% oil recovery advantage over Hot Water Flotation, providing good agglomeration conditions were established. This is the key for a successful application of the process. Sand Reduction at ambient temperature with good quality Area B oil sands is feasible, but is not as effective with some marginal and poorer grades of oil sands. However, it was shown in these preliminary studies by suitably adjusting conditions of: (1) temperature, (2) equipment parameters e.g., shear, (3) agglomerate recycle, (4) chemical treatment, and (5) oil sand blending that most oil sands could probably be made to process well in the Sand Reduction Process. These variables need to be evaluated in further pilot plant studies on site.

8-5 Agglomerate Processing

The Sand Reduction in which the resulting oil-sand-water mixture is fed directly to fluid coking, needs to be in heat balance. A key agglomerate quality is low water.

8-5-1 Water Content

In the laboratory submerged screening technique, the agglomerate is removed from the screen, weighed wet, dried in an oven at 220°F, and weighed again to determine the water content. Just prior to weighing wet, any surface free water is drained off. The average water contents of agglomerates measured, in the various Sand Reduction types of experiments as discussed before, are summarized below:

Average Water Content of Agglomerate

(approx. 25 Experiments Averaged)

	Tar Sand	**average Wt % Water**
Operation	**charge(g)**	**Content of Agglomerate**
Mortar and Pestle	25	22
Batch Mixers	400-600	13
Continuous Mixers	-	12
Tumblers/Ball Mills	100	3

The higher water contents of the agglomerates from mortar and pestle studies was a physical effect attributed to the larger surface area of the oil phase to retain free surface water. This is supported by the lower water content data obtained in batch mixing operations using larger charges.

Table 8-12

Process Comparison on Good Quality Oil Sands Area B : 10-7 Grade

	Hot Water Flotation	Sand Reduction
Temperature, °F	185	~70
Producer	Froth	Agglomerate
Froth/Agglomerate		
Composition		
-Water wt%	(27)	12
-Solids wt%	(14)	28
-Oil wt%	(59)	60
-w/o Ratio	(0.23)	0.46
-s/o Ratio	(0.45)	0.20
Sand Reduction w/o %	(97)	88
Oil Recovery wt % in		
-Froth or Agglomerate	(93)	99
-Solids i.e., loss	(7)	~1

8-5-2 Coking Agglomerates

The heat requirement for preheating an agglomerate to a typical coking temperature is compared in Table 8-14 with fluid coking of the tar sand feed and the oil froth produced by hot water formation. It can be seen that on an average, agglomerates require less coke to be burnt to stay in heat balance. As the coke produced might be about 15 wt% based on oil, it is, therefore, conceivable that the agglomerate from sand reduction with <9 wt % water content, could be fed directly, and that the heat balance could be maintained. The relationship of heat requirement to water and solids in the coker feed, together with the data in Table 8-14 are shown diagramatically in Figure 8-21. The magnitude of the numbers, however, indicates that there is considerable incentive to continuously reduce the water content of the feed to a coker. Tumbler-ball mill experiments clearly showed, Table 8-13, that suitable water contents with both good and poor quality oil sands can be obtained that are acceptable for direct coking of agglomerates.

8-6 Economics and Conclusions

Imperial Oil Ltd. and Cities Service Athabasca Incorporation both carried out independent economic studies in 1961 based on the original investigations of Sand Reduction. C.F. Brown also conducted an independent evaluation. The basis was the same as Hot Water Flotation in that the extraction plant was integrated with upgrading and remote from mining.

The results in all these comparisons looked attractive provided all types of tar sands could be processed at high oil recoveries and with good product qualities. No credits were given to Sand Reduction for the potential to integrate the process with mining, resulting in substantial savings from reduced oil sands handling and solids disposal.

8-7 Summary

In process comparisons, the Sand Reduction oil recoveries were better by 5-10%, than those of Hot Water Flotation. Hence, Sand Reduction appeared more than competitive with both good and poor quality tar sands provided in the latter case, oil particle agglomeration can be achieved and maintained on a continuous commercial scale for good separation.

This appeared quite feasible by using either one or combinations of the following techniques: (1) poor/good tar sand blends in about a 25/75 ratio (2) internal recycle of agglomerate or a tar binder, (3) pH-Chemical additives, and (4) increasing temperature slightly from the usual ambient operating conditions. This latter factor decreased the oil viscosity that is a controlling factor in effecting simultaneous sand reduction - bitumen agglomeration.

It should also be noted that marginal quality tar sands occur far less frequently than good quality oil sands in the CSA site, and that these types of oil sands can be agglomerated by simple adjustment of the mixer operating parameter, eg. weir height, paddles, water usage, etc. And, in the case of poor quality tar sands, combination techniques as discussed above can be used. Fur-

Table 8-13

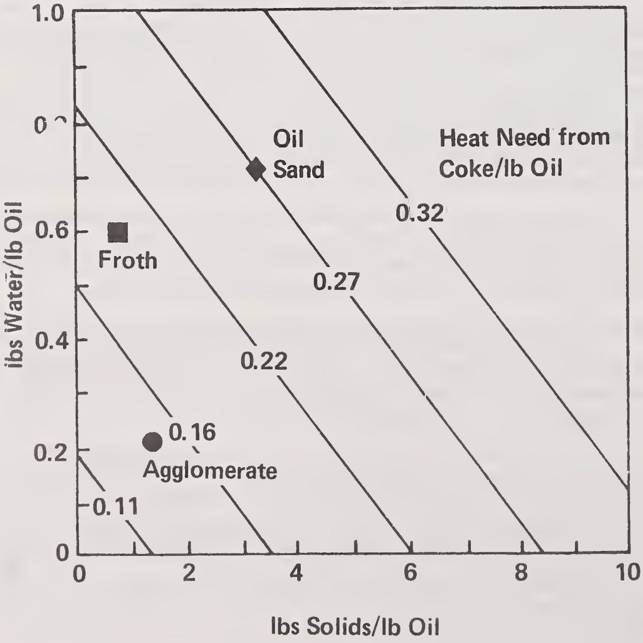
Sand Reduction of Maginal Quality Oil Sands for Low Water Content Agglomerates

Tar Sand Area (Hole)	B			D (9)			D (10)		
Test Locations	Sarnia	Ottawa [(1)]		Sarnia	Ottawa [(1)]		Sarnia	Ottawa [(1)]	
No. of Runs (Averaged)	2	2	2	2	2	3	2	2	4
Equipment	Kneader	Tumbler		Kneader	Tumbler		Kneader	Tumbler	
Temperature, °F	70	Unknown		90	Unknown		90	Unknown	
Agglom. Recycle, % on Oil	20(3)	0	~50(4)	20(2)	0	50	20	0	50
Chemical Treat				0.1% NaTPP	Unknown		0.1% NaTPP	Unknown	
Composition									
Water wt%	9	5	1.5	12	2.5	3	13	1.5	2.5
Solids wt%	26	30	24	28	26.5	14	29	35.5	15
Oil wt%	65	65	74.5	60	71	83	58	63	82.5
w/o Ratio	0.14	0.08	0.02	0.20	0.033	0.034	0.22	0.02	0.03
s/o Ratio	0.40	0.46	0.33	0.47	0.38	0.18	0.50	0.56	0.18
Yields, wt%									
Agglomerate	21	23	19	18	17	13	15	19	17.5
Tailings	79	77	81	82	83	87	85	81	82.5
Oil Recovery									
Agglomerate	98	-	98	98	-	95.5	98	-	97
Solids i.e., loss	2	-	2	2	-	4.5	2	-	3

(1) Data generated on low water agglomeration for Imperial by consultant Dr. I.R. Puddington.
(2) Non optimized conditions.
(3) Backed out of results.
(4) Estimated.

Figure 8-21

Coking



ther, recycle of an oil binder to build agglomerate size with tumbling that shapes the agglomerates with balls, thereby squeezing out water, has the ability to produce an agglomerate product for direct coking in an operation that will be in heat balance. Alternately, the agglomerate that contains substantially more solids can be just as easily upgraded to bitumen by solvent solution as froth, see Section 10.

Hence, the potential advantages of Sand Reduction over Hot Water Flotation, for further evaluation, development, and scale-up are:

- *lower operating temperature/less energy needs.*
- *higher oil recoveries/better resource utilization.*
- *relative drier agglomerate/less emulsification.*
- *tolerance to clays in recycle water and oil sands.*
- *no recycle water treatment except settling.*
- *less disposal and pond needs.*

The most convenient method of separating the sand and agglomerates, that was found, developed, and used in the continuous pilot unit demonstrations of the Sand Reduction Process, was submerged rotary screening. Although the commercial application of this separation techniques appears feasible, it does have the disadvantages of moving parts, low screen utilization, and the need to clean the screen when in operation. A more attractive method of separating agglomerates that might be developed based on several preliminary successful laboratory experiments is Cold Water Flotation - Sand Reduction. Possibly a combination of these separation techniques may be needed in application to handle all types of oil sands.

Unfortunately, at the time that Sand Reduction was extending the process development stage, Syncrude converted from a research to a commercially focused project, and Sand Reduction technology was shelved.

Table 8-14

Comparison of Heat Requirements for Direct Fluid Coking of Feed and Products

Composition, Wt%	Good Grade Tar Sands (No. 11)	Froth from Hot Water Separation	Agglomerate from Sand Reduction	
			Batch	Ball Mill
Oil	14	59	58	74.5
Solids	80	4	27	23.0
Water	6	37	15	2.5
Composition per lb of Oil				
Oil	1	1	1	1
Solids	5.71	0.07	0.47	0.28
Water	0.43	0.63	0.26	0.03
Heat Required to Heat Feed Containing 1 lb of Oil(1)				
Oil	717	717	717	717
Solids	1216	15	100	60
Water	667	977	403	50
Total	**2600**	**1709**	**1220**	**827**
lb of Coke/lb of Oil to Product Heat Requirement(2)	0.282	0.185	0.132	0.090

(1) Using heat requirement values W.S. Peterson and P.E. Gishler, The Fluidized Solids Technique Applies to Alberta Oil Sands Problem. National Research Council of Canada Report: - Feed at 32°F, still products at 932°F, burner at 1300°F. No heat recovery. 1 lb Oil = 717 BTU. 1 lb Sand = 213 BTU. 1 lb Water = 1550 BTU.

(2) At 9230 BTU/lb net heat release.

9

SOLVENT DILUTION

The process of solvent dilution for separation of solid and water contaminants from both hot water froth and cold water agglomerates, as well as from oil sands per se, involves:-

- (1) selection of solvent and mixing of the solvent with the oil/water/solid mixture to form a continuous oil/solvent phase.
- (2) removal of the oil-solvent overhead containing essentially all of the oil and the solvent with minimum contamination by water and solids, that is processed further for an oil product as well as solvent recovery and recycle, and,
- (3) clean separation of the solids and water contaminants of the oil phase by either centrifuging, or gravity settling, or a modified technique that results in minimum solvent/oil loss.
- (4) solvent recovery from separated solids.

This type of separation can be readily demonstrated in the laboratory. However, it is difficult to carry out precise separations and quantitative measurements on the system, because as soon as a system of oil/water/solids is diluted with solvent it will separate into four distinct phases, Figure 9-1. This separation generally involves three main sub processes that occur simultaneously and that need to be defined in developing a solvent dilution process design. These are:

- *(a) settling of solids and water in the oil-solvent phase to the water interface,*
- *(b) transferring of water-wet solids across the skin or membrane like emulsion that accumulates at the oil/water interface and,*
- *(c) minimizing oil/solvent losses by avoiding occlusion in transferring solids into the water phase.*

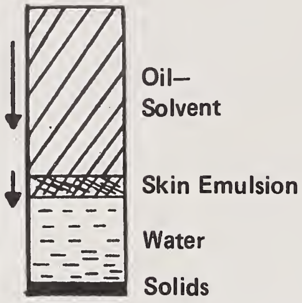
Figure 9-1

Problem of Dilution and Settling as a Froth Upgrading Process

Separation Problem

1. Settling of Solids and Water in the Oil–Solvent Phase
2. Transfer of Water–Wet Solids Across Resistance Skin Emulsion Interface
3. Minimize Oil Loss

Four Phase System



Approach to Problem

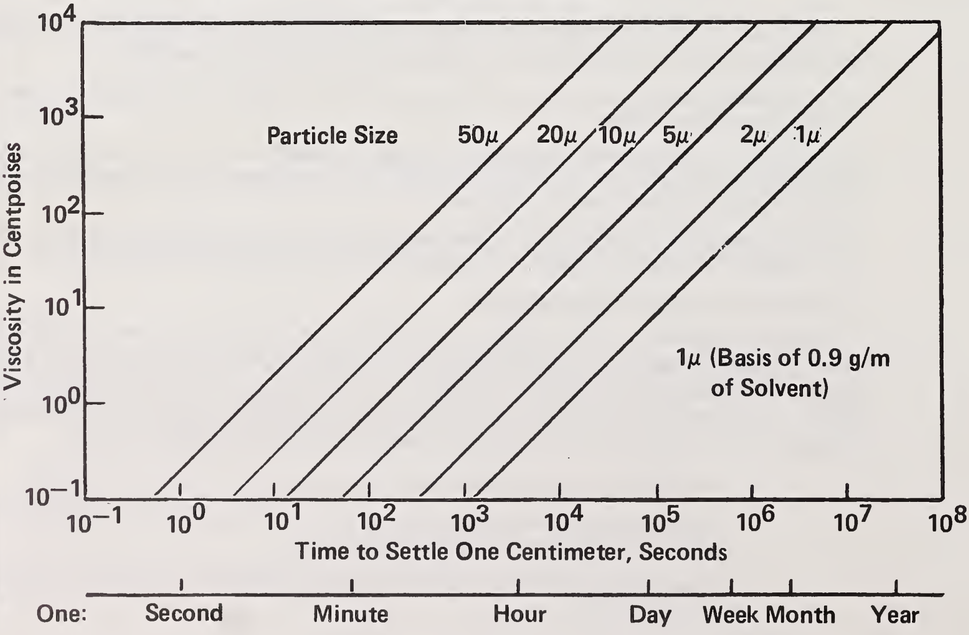
1. Measurement of Physical Properties and Application of Stokes Law
2. Mechanical and Chemical Aids
3. Chemical Additives

Application of Stokes Law to Settling

(Basis: 0.8 g/ml Solvent)

$$t = \frac{2gl^2 (\ell 3 \;\; \ell 8)}{9 \eta}$$

Where t = Time in Seconds, g = Gravitational Constant, 1 = Length of Fall in mm r = Radius of Particle in mm, ℓ 3 = Density of Particle g/ml, ℓ 8 = Density of Liquid Phase g/ml, η = Viscosity of Liquid Phase in Centipoises



The main technical problem is achieving clean separation of solvent/oil and water phases, and the clean transfer of solids through the interface. A satisfactory solution will greatly improve the poor economics of past solvent dilution processing studies that is attributed mostly to high solvent losses.

Hence some laboratory studies were carried out in an attempt to understand the reasons that might have been responsible for low oil recoveries found in past (Royalite and Cities Service) pilot studies of solvent dilution and settling and to devise better methods of increased efficiency. These studies are developed stepwise in this Section.

9-1 Settling Rates

The problem of settling of solids and water in the solvent-oil phase can be treated effectively by the application of Stokes Law, Figure 9-1. The measurement of certain physical properties are required in order to substitute and calculate the rate of settling that will take place in the separation system. The physical properties required are solution viscosity, and gravity, as well as particle size and particle gravity. Considering these variables, the particle gravity can be assigned values of about 2.6 g/ml for silica and about 2.2 g/ml for clays. This assumption is based on the fact that solids in the froth are mainly quartz and clay minerals, i.e. illite and kaolin. Solution gravity can also be assigned an initial value of 0.8 g/ml, and its effect calculated subsequently. Solving the equation for particle sizes over the ranges 1 to 50μ, gave a linear log parameter of particle size on a log vs log plot of viscosity and time to settle one centimeter in seconds. Recalculation for a solvent having a gravity of 0.9 g/ml would increase the time by only 6%. In contrast, the degree of water wetting of solids has a significant effect, that was taken into account and appropriated adjustments made in settling rate studies. The relationship shows that to remove small size particles by settling will be extremely difficult on a practical scale. In design of process equipment, a time limit in the separation will have to be imposed and residual contaminants taken out in the next process step.

All measured settling rates in diluted froth were high, i.e. <1 hour, when the major of contaminants had accumulated on the solvent/oil-water interface. These results agree reasonably well with predictions, but involved some assumptions on the degree of solid/water association, and on the measured size distribution of solids or agglomerated solids using microscopic techniques, e.g. mostly >3 μm.

9-1-1 Effect of Oil

The viscosity of oil is the key variable in separation by solvent dilution and settling. The viscosity of the oil is well-known to be extremely high at room temperature. Raising the temperature however markedly reduces the viscosity of the oil as is shown in Figure 9-4. The data for three typical separated oils from the Mildred Lake area are shown. In general Area B type oil is more viscous than a Mildred Lake composite obtained by blending various samples of Hole 9, Hole 11, and Area B oils. Beaver River oil has been found to be even less viscous than the Mildred Lake composite. The Beaver River oil was used in all further dilution settling studies.

9-1-2 Solvent Selection

Viscosity temperature measurements were made on a number of pure hydrocarbon and typical petroleum fractions and compare with that for oil, Figure 9-2. The viscosity in centipoises that is plotted against temperature for these various solvents gave very shallow curves, approaching 0.1 centipoise. This also illustrates that the process temperature is more important for reducing the viscosity of the oil.

Inspections on the solvents and mixtures of oil/solvent are summarized in Table 9-1. Gravity and viscosity temperature relationships are plotted in Figure 9-3. It will be noted that almost a linear relationship is evident in this type of plot thus enabling ready interpolation of the data to be made. This data however is limited to 140°F, but similar plots are attainable for other temperatures. This data was obtained for calculating settling in evaluating rates of particle transfer across the interface.

A typical correlation plot of these data is shown in Figure 9-4 for Athabasca virgin and coker gas oils, and deodourized varsol as example solvents. In this plot using the ASTM linear

Figure 9-2

Comparison of Viscosity-Temperature Relationships of Oil and Various Solvents

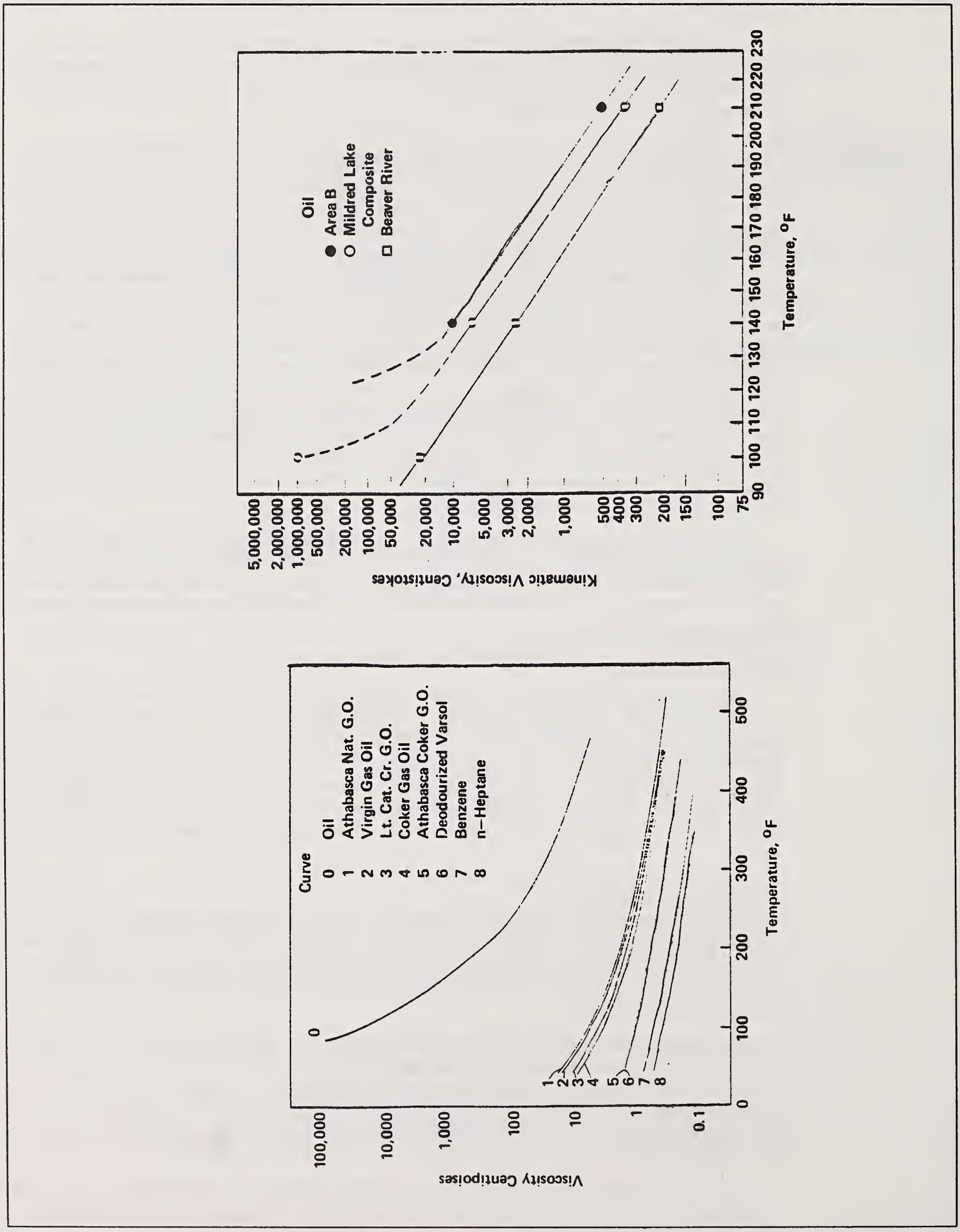


Table 9-1

Inspection on Solvents and Solvent Mixtures

Solvent Inspections	Gravity °API at 60°F	Boiling Point, °F	Molecular Weight	Kinematic Viscosity cs at 140°F	Interfacial Tension Dynes per cm at 75°F
Pure Hydrocarbons					
n-Heptane	73.2	209	100.2	0.46	37.1
Heptane-1	71.5	201	98.2	-	-
Cyclohexane	50.1	178	34.2	0.72	45.1
Methylcyclohexane	52.0	212	98.2	0.66	43.8
1,2 Dimethylcyclohexane	50.1	248	112.2	0.68	44.5
Kylene	30.8	292	106.2	0.56	37.6
Benzene	29.5	176	78.1	0.52	-
Decalin	26.4	382	138.3	1.66	41.3
Tetralin	14.1	405	132.2	1.26	22.1
Hydrocarbon Mixtures					
Deodourized Varsol	46.9	360 - 410	151	0.99	42.4
Athabasca Coker Gas Oil	34.3	230 - 650	151	0.95	10.7
Virgin Gas Oil	31.8	400 - 680	228	2.86	30.0
Coker Gas Oil	30.0	360 - 720	218	2.29	16.2
Solvesso #150	27.4	370 - 420	140	-	-
Hydrotreated Atha. Coker G.O.	25.9	-	142(Est)	-	-
Lt. Cat. Cracked Gas Oil	24.9	430 - 660	210	2.40	28.0
Athabasca Natural Gas Oil	24.8	470 - 630	205	3.62	23.1
Heavy Aromatic Naphtha	20.5	340 - 540	160	-	-

(1) FLA analyses
(2) Based on carbon type in molecule

Oil in Mixture, wt%	---------- 10% ----------		---------- 50% ----------	
Inspections	**Gravity °API at 60°F**	**Kinematic Viscosity cs at 140°F**	**Gravity °API at 60°F**	**Kinematic Viscosity cs at 140°F**
Solvent				
(a) **Pure Hydrocarbons**				
n-Heptane	68.2	0.53	38.2	3.02
Cyclohexane	46.0	0.98	28.8	5.69
Methylcyclohexane	47.2	0.83	29.6	4.69
1,2 Dimethylcyclohexane	45.8	0.92	28.6	5.15
Xylene	29.3	0.69	20.0	3.68
Benzene	25.8	0.70	19.0	3.97
Decalin	24.6	2.25	17.5	12.80
Tetralin	13.5	1.74	11.4	9.98
(b) **Hydrocarbon Mixtures**				
Deodourized Varsol	43.1	1.30	26.3	7.27
Athabasca Coker Gas Oil	29.7	1.29	20.8	7.65
Virgin Gas Oil	30.5	3.85	18.0	30.38
Coker Gas Oil	29.7	3.20	18.8	17.27
Lt. Cat. Cracked Gas Oil	23.5	3.30	16.4	19.20
Athabasca Natural Gas Oil	23.0	4.90	14.8	30.70

Figure 9-3

Viscosities of Oil-Solvent Mixtures

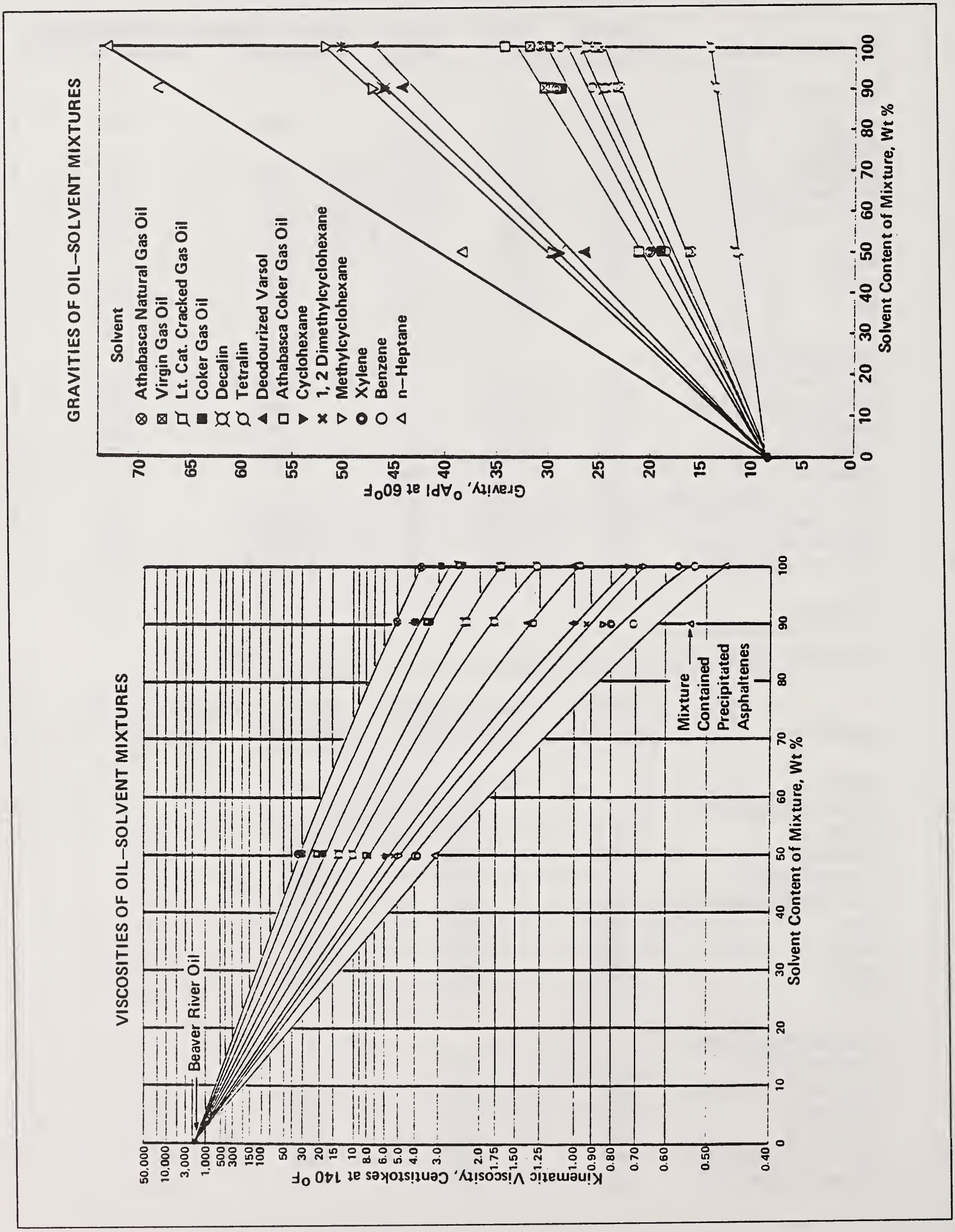
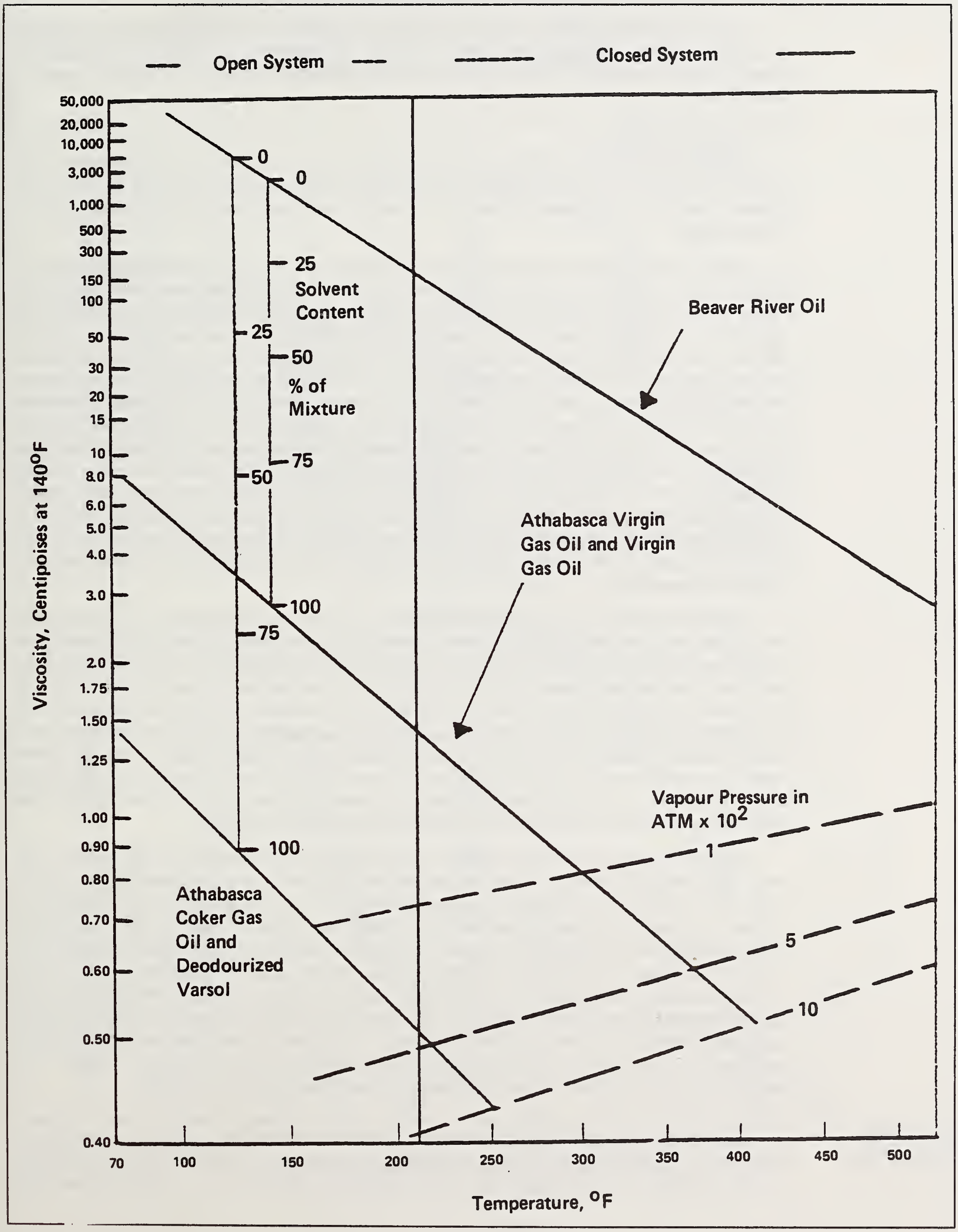


Figure 9-4

Viscosity-Temperature Relationship for Solvent Dilution of Oil Showing Vapour Pressure Limitations



viscosity temperature relationship, solvent to oil ratios can be plotted vertically. Also shown is the effect of vapour pressure, which contributes a process limitation for the system at higher temperatures. Yet another variable shown is pressure in that below 212°F an open system can be utilized, and above this temperature a closed or pressure system is needed.

Lowest solvent/oil viscosity is the most important property to achieve high rates of settling of solids and water contaminants. Higher economic temperatures of separation governed by vapour pressure limitations is the other important process factor to reduce the oil phase viscosity to a minimum.

9-1-3 Solution Rates

It had been observed in earlier experiments that sludge formation increased markedly with reduced mixing time. As sludge formation was the main cause of large solvent/oil losses in past Mildred Lake bench unit operations, some consideration was therefore given to solvent type effects in mixing.

Experimentally, mixing was carried out at constant temperature by constant stirring only in the upper solvent phase in contact with a lower oil phase. The solvent phase was sampled at regular time intervals and gravity determinations were made using a Davidson Graviometer. The oil content was then estimated from the corresponding viscosity and correlation discussed in the previous Section 9-1-2. A typical set of data for a pure hydrocarbon and a petroleum fraction are shown in Figure 9-5. The final experimental point was checked by decanting the solvent phase and weighing the final amount of undissolved oil. The data obtained in this arbitrary procedure defined what appeared to be a slope or rate of solution, which has been expressed as oil percent per minute up to a time T_e defined as the equilibrium time in minutes. At this time the rate of oil dissolving in the solvent appeared to markedly decrease, and was about the same as that measured at the end of the experimental time T. This treatment of the experimental data proved satisfactory in that relative arbitrary values for the equilibrium time T_e, the percent of oil dissolved at equilibrium, and the rate of solution were obtained. The numerical results of this treatment of the data are summarized in Table 9-2, together with corresponding viscosities and solvent power parameters.

The rate of solution is plotted against solvent power at the top of Figure 9-6. It appears that the solution rate was independent of solvent power, but its reciprocal showed a fair correlation with solvent viscosity. However, the time to reach oil-solvent equilibrium T_e in these tests correlated well with Solvent Power as shown in Figure 9-6. Further, the oil percent undissolved at equilibrium or sludge formation tendency of the mixture correlated with the viscosity of the solvent, shown in Figure 9-7. The percent oil undissolved at equilibrium is taken as a measure of a sludge forming tendency, in that undissolved oil would not necessarily appear in the oil solvent phase, but would tend to sink as a sludge and constitute an oil loss with separated solids in the water phase. Thus, a sludge forming tendency in solvent dilution could very well result from either the solvent used in the process or from insufficient time in mixing.

In summary, these preliminary studies of the rate of mixing or rate of solution indicate that some of the physical variables of the system play an important role in the process. Notably viscosity that correlates with the rate of mixing or solution in percent of oil dissolved in different solvents per minute at equivalent solvent to oil weight ratio. Also, the time to reach an arbitrary solution equilibrium was found to correlate with the Solvent Power of the solvent. Further, increasing the viscosity of the solvent was found to decrease the amount of oil dissolved in the solvent at the arbitrary test equilibrium. This effect has been termed a sludge forming tendency in that undissolved oil can result in sludge, as was observed in previous studies. However, the test itself is mild relative to what might be achieved in a high speed mixing operation and is more a measure of diffusion rates of constituents. However, further work is indicated to explore the variables in mixing solvents with froth containing other phases of water and solids.

9-2 Froth Upgrading

Many small scale exploratory studies have been carried out on froth upgrading. These investigations were directed at defining the more important factor in separation, and the effect of chemical additives. A further objective was to develop a separation system which might be used

Figure 9-5

Solution Rates of Beaver River Oil & Treatment of Solution Rate Data

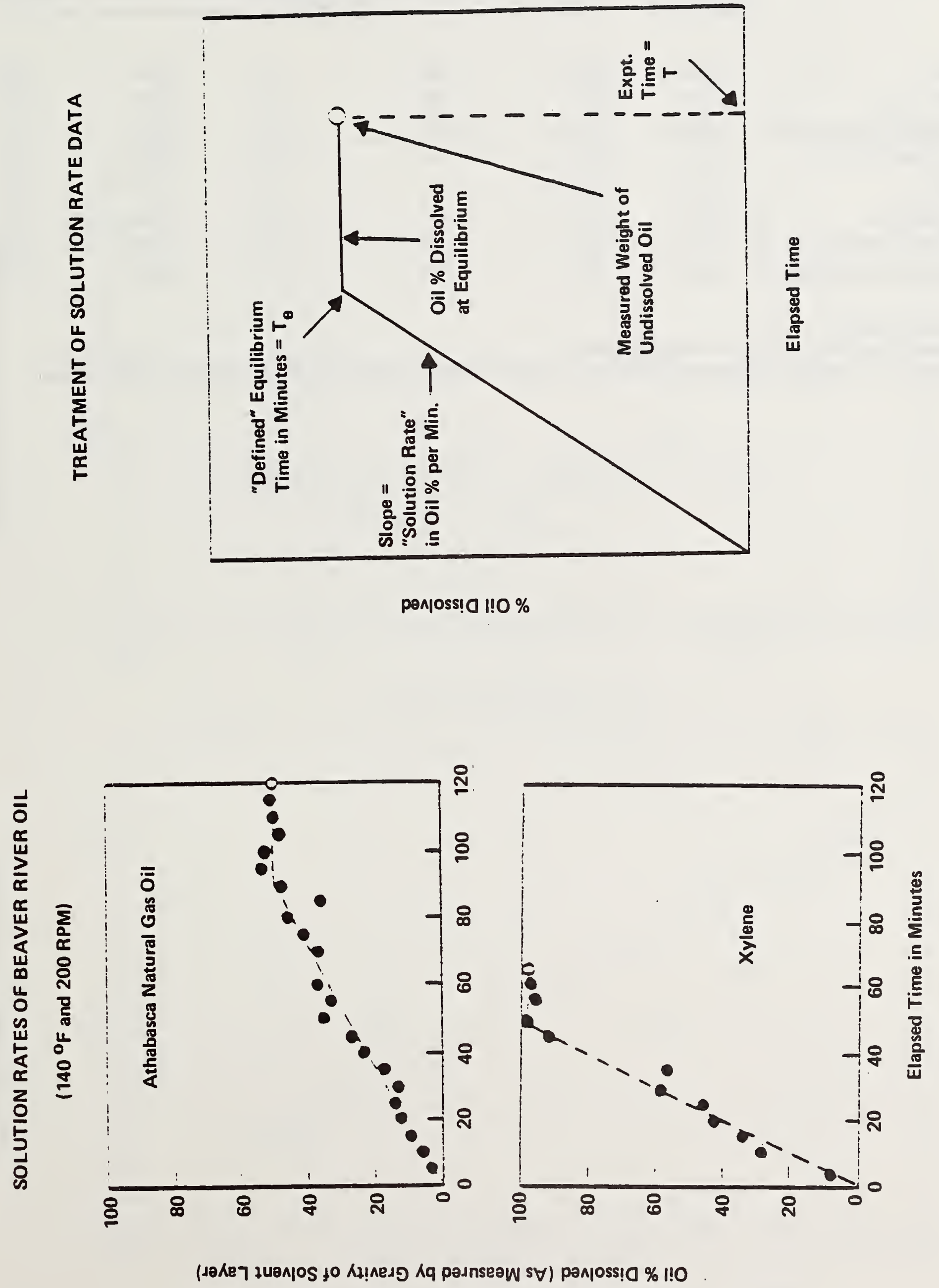


Table 9-2

Solution Rate Data

Solvent	Solvent Power(1)	Kinematic Viscosity,cs	Oil % Dissolved at Equilibrium(2)	Equilibrium Time, Mins(3)	Solution Rate %/Min	1 Solution Rate
	(At 70°F)	(At 140°F)				
Xylene	+2.14	0.56	98	48	2.04	0.49
Cyclohexane	+0.48	0.72	94	90	0.99	1.01
Athabasca Coker Gas Oil	+0.82	0.95	75	90	0.83	1.21
Deodourized Varsol	-0.21	0.99	74	112	0.66	1.52
Decalin	+1.79	1.66	67	70	0.96	1.04
Coker Gas Oil	+0.18	2.29	61	103	0.59	1.70
Light Cat. Cracked Gas Oil	+1.28	2.40	66	85	0.78	1.28
Athabasca Natural Gas Oil	+0.99	3.62	50	90	0.56	1.79

(1) Measured as Cot θv

(2) Measured by decanting solvent layer and weighing residue.

(3) Intercept of oil % dissolved at equilibrium and solution rate in oil %/min dissolved as measured by gravity determinations on solvent-oil phase.

Figure 9-6

Effect of Solvent Power and Viscosity on Solution Rate of Oil at 140 °F

(See Figure 9–7 for Symbol Key)

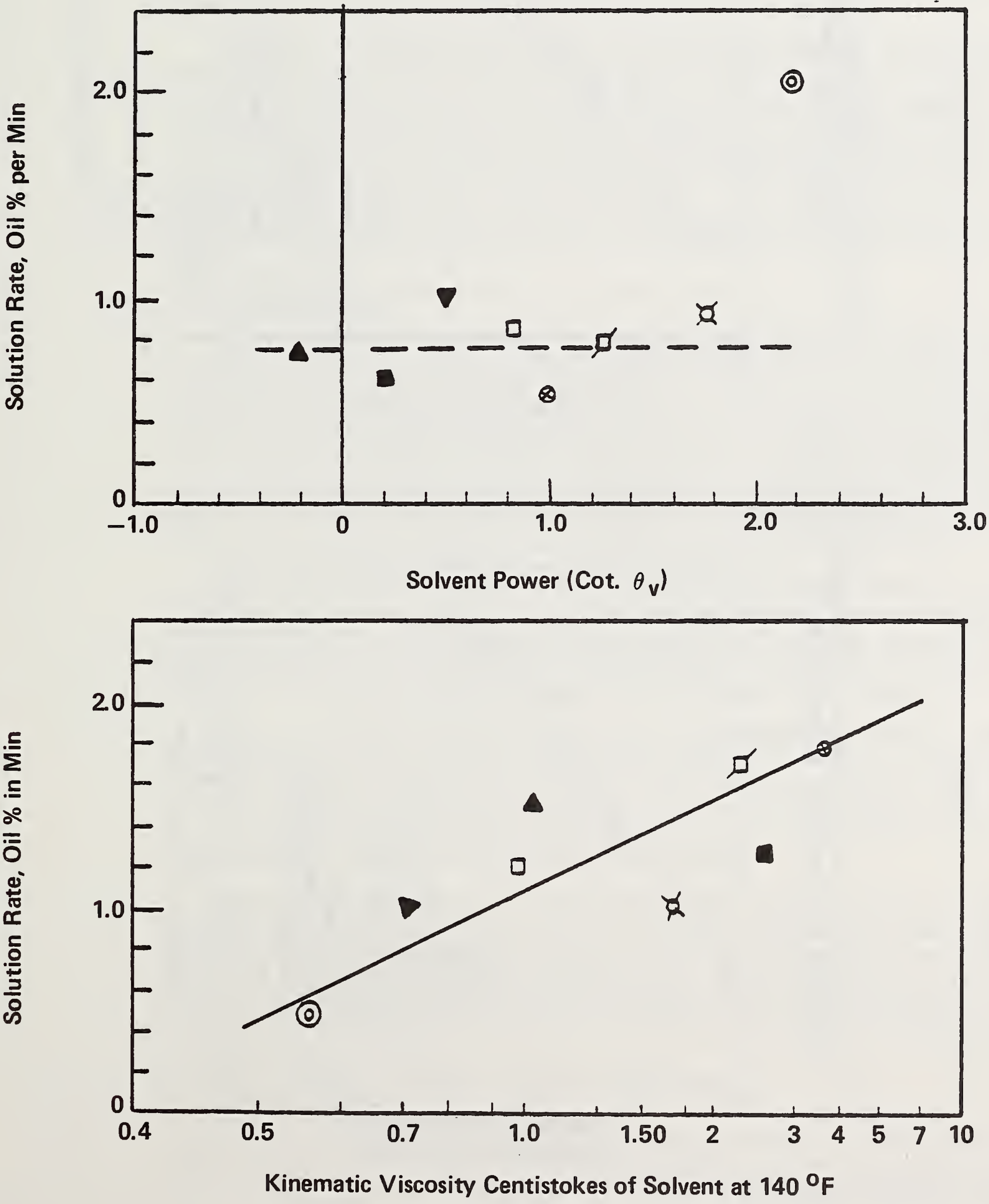
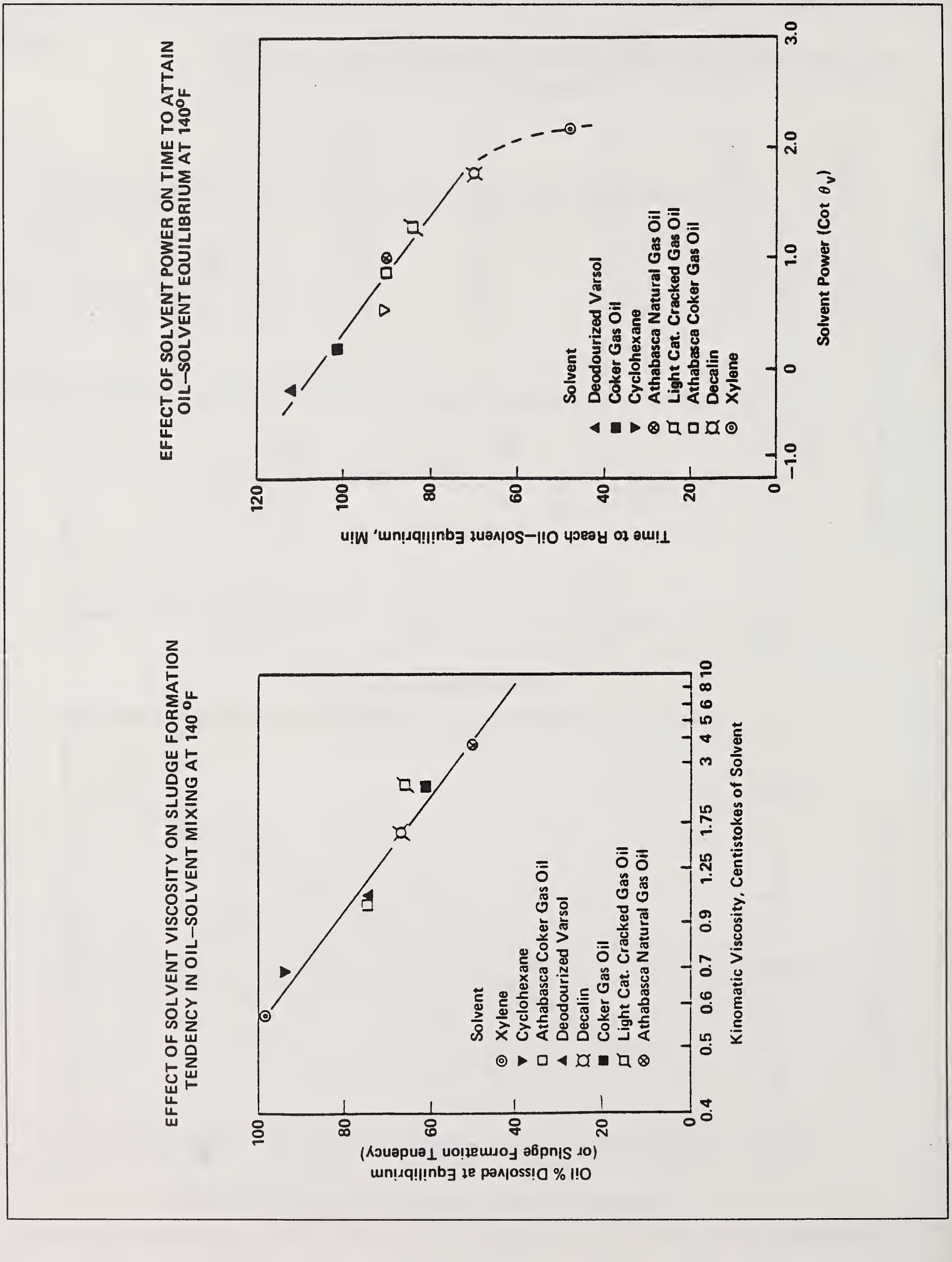


Figure 9-7

Effect of Solvent Viscosity on Sludge Formation Tendency in Oil-Solvent Mixing at 140 °F



to quantitatively evaluate the effects of additives. These studies explored briefly the approaches listed in Table 9-3 and definition of terms are shown diagrammatically in Figure 9-8.

Separations in water often result in several phases. It should be noted here that a mixture of solids-water-oil-solvent which sinks to the bottom of the system has been called *sludge* (brown-grey-black in appearance - under the microscope a system of skins); and a similar mixture which appears at the oil-solvent/water interface or is suspended in the oil-solvent phase has been called *emulsion*. Thus, these terms are almost synonymous.

The conditions used to effect a separation can also significantly affect the result. For example, inadequate mixing can result in large sludge volume. High speed mixing can effect large emulsion volume (more water), particularly at the temperatures used of 150-180°F. Low mixing intensity has been found to be preferable, over a long time.

The sequence of addition of components to the system is also important. No effect of adding solid inorganic agents before or after solvent addition has been observed. The addition or organic agents (surfactants) should be made after solvent and particularly after inorganic agents have been added, as antagonistic effects have been observed, e.g., re-emulsification of water-wet solids when both inorganic and organic have been added simultaneously. Standardized mixing and accurate separation of phases for quantitative evaluation are difficult problems. Most of the exploratory experiments discussed in this section are either qualitative or semiquantitative, and in each case an effect is recorded in reference to a blank experiment without the additive under study.

9-2-1 Water Washing

Considerable solids can be removed from the froth formed with aeration by water washing. The solids removed by this process are mainly sand and clay. Progressive froth washing studies have shown heavy minerals to be retained more in the oil phase. In one example of water washing, 52% of the total solids were removed. Only very small quantities of heavy minerals, ~3%,were removed and these were found to be mainly siderite, leucoxene and hematite, with some tourmaline and kyanite. No zircon was observed using UV fluorescence in the first washings. Only in the later washings were trace zircon and ilmenite evident. Froth washing with solutions of sodium salts of weak acids showed substantial improvements in solids reduction. The results were similar to those to be discussed under inorganic additives in this section.

One method to reduce the solids content of the froth is to minimize aeration in primary separation. Froth from this type of hot water flotation separation does not respond so noticeably to water washing now the excess solids (sand and clay) have be reduced. Preliminary water washing studies at high mixing intensity with froths generated without air in the separation step removed only very small quantities of a fine white-brown suspension in the water phase.

Addition of inorganic chemicals improves the solids reduction. Particularly, sodium tripolyphosphate has been found to be the most effective additive with this type of froth. It may be tentatively concluded here that Froth Washing is only useful when solids are being floated into and/or entrained in the froth by aeration and/or by high agitation in separation. Froth washing preferably removes these entrained solids and does not reduce those solids that are more closely associated with the oil, e.g. heavy minerals, etc. Figure 9-9.

This is substantiated by analyses of water washed froth solids. For example a sample of roller dewatered froth solids received from CSAI exhibited a high content of heavy minerals 59%. The 36% of heavy minerals that separated rapidly in tetrabromoethane were granular, greater than 325 US mesh and exhibited a high content of zircon and ilmenite. However, fines separated after long standing amounting to 23% of separated heavy minerals showed only a trace of zircon. These fines appear to be comprised more of heavy minerals with low hardness values, than other minerals, e.g. zircon.

9-2-2 Solvent Dilution

With just solvent addition (no water) only small amounts of water wet solids, mainly silica (sand) are removed. Other mineral types are present mainly as a settled sludge (grey). A small amount of the minerals are also suspended in the oil phase. Sodium tripolyphosphate treatment

Table 9-3

Froth Upgrading Techniques Studied

A. **Froth (as produced) Washing**
1. Water (only)
2. Solution Washing
3. Additives and Settling anhydrous
4. Additives and Settling in water or salt solution

B. **Froth Solvent Dilution***
1. Additives - Anhydrous
2. Additives - with water (sol^{n})
3. Decoating with emulsion treating
4. Separation with water and sludge freaking
5. Dilution Settling

* Also applies to agglomerate from sand reduction.

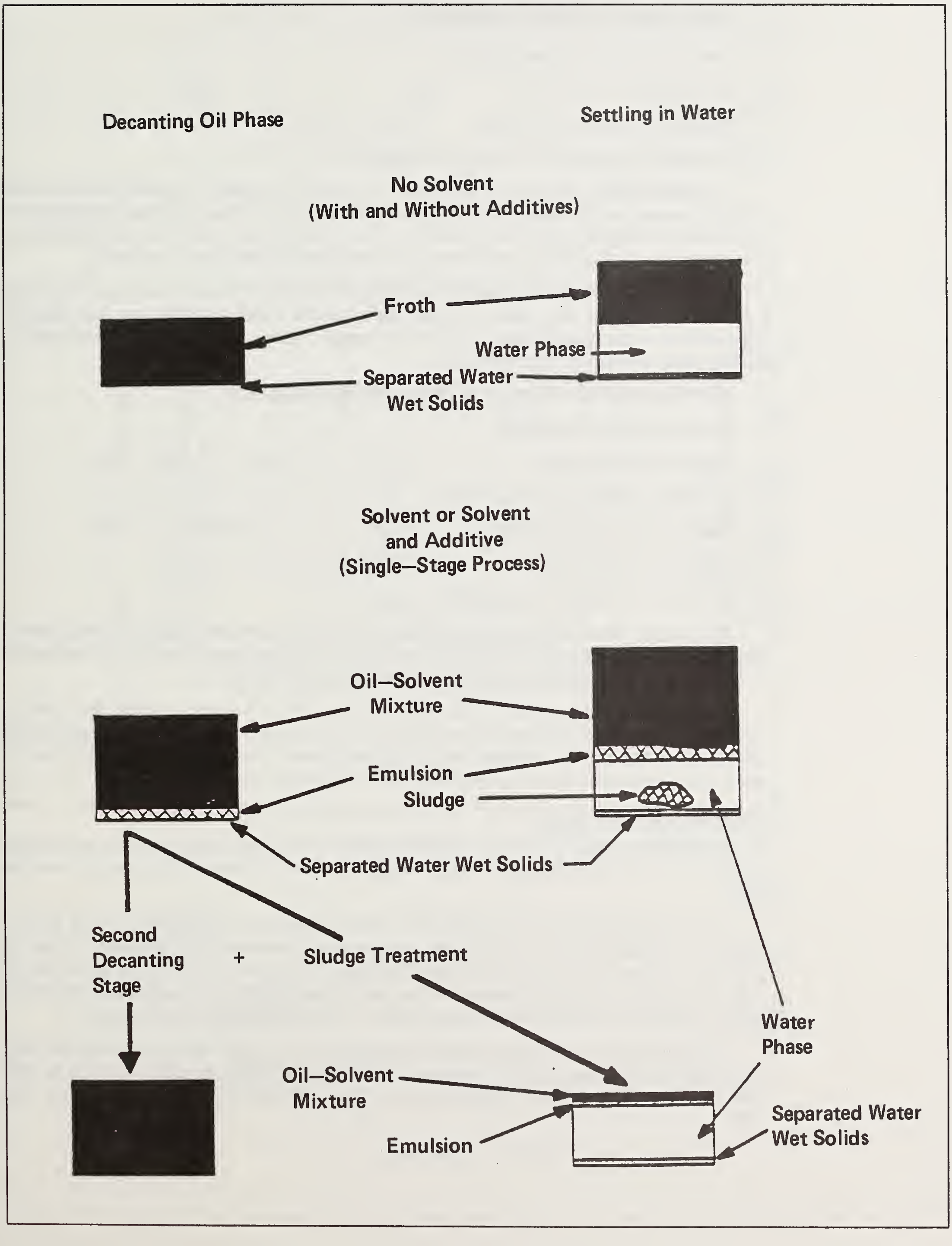
Note: - Criteria of Solvent Separation to Compare Additives

1. Amount of separation of water wet solids
2. Amount and rate of separation of sludge
3. Sludge volume settled
4. Emulsion volume at oil-solvent/water interface
5. Clear interface - possibility of separating phases
6. Water reduction in the oil phase
7. Oil recovery in oil-solvent mixture or emulsion (recoverable)
8. Solvent loss

It is not always possible to integrate all observations in one single conclusion, and in the ensuing discussion the criteria selected for making a comparison will be pointed out.

Figure 9-8

Froth Upgrading Techniques Studies (Shown as Relative Volume for Upgrading Beaver Creek Froth at 150 °F)



(1 wt% on froth) followed by solvent dilution removed more water-wet solids (some heavy minerals) than solvent alone. The emulsion-sludge is still a larger phase and a "problem" to good separation with froths formed with minimum aeration. The criteria of sludge volume that settled in about two hours, was used to make the comparison.

EFFECT OF SOLVENT ADDITION

(Varsol 3139 and no Water in Sepn)

Solvent Ratio Vol/Vol of Oil	0.1	0.3	0.45	0.6	0.9	1.2	2.9	5.8
Emulsion Volume After Settling	N	S	M-L	L	L	L	L	L

N = None, S = Small, M = Medium, L = Large

The effect of solvent dilution only appears to be more attributable to gravity difference and viscosity changes aiding settling, than selective solvent effects. Perhaps the more aromatic solvents were very slightly better, and paraffinic solvents did appear to have less compatibility or solvent power, which is what would be expected from previous observation, Section 2.

As the solvent to oil ratio increased more sludge settled out and more oil-solvent occurred as a distinct upper phase. Very little if any further water-wet solids separated out. The effect of water addition to the system mainly results in floating the system, but facilitates the separation of the very small amounts of water-wet solids.

EFFECT OF SODIUM TRIPOLYPHOSPHATE ADDITION

(No water added in separation)

Additive, Wt% on Froth	1.0	-	0.25	1.0	2.5	5.0
Solvent to Oil Ratio, Vol/Vol of Oil	0		---------------- 1.2 -----------			
Emulsion Volume After Settling	N	L	M	S-M	S	VS
Amount of Water-Wet Solids	S-M	N	S	S-M	M	L

N = None, S = Small, M = Medium, L = Large

The general effect of solvent addition found with the Beaver Creek Bench #1 froth (formed without aeration) in separation, paralleled previous studies of solvent-oil ratio on the separation of froths (formed with aeration) and agglomerates from Sand Reduction.

A minimum solvent (varsol) to oil ratio of about 0.7 is required to effect the optimum separation of a distinct emulsion phase. Higher solvent-oil ratios result in only slightly better separations at higher rates of separation. The higher solvent to oil ratio of 1.2 was selected for use in subsequent additive studies to achieve rapid and efficient separations.

9-2-3 Inorganic Additives

The effects of adding different inorganic additives have been explored without the addition of solvent. The criteria (#1) used to make comparisons was the amount of separated water-wet solids.

An example of a study with a froth formed with aeration and inorganic addition is given in Table 9.4. It should be noted that the more separation of water-wet solids (criteria #1) then the less sludge volume that occurs (criteria #3), and more water separates from the oil phase with the water-wet solids (criteria #6). It was found that the polyphosphates were particularly effective in order of effectiveness sodium hexametaphosphate > tripolyphosphate > pyrophosphate.

A pH effect again is probably operative, although it is very difficult to measure this value. The pH effect is evidenced by acid addition to overcome the alkaline condition of the other additives and further high alkaline pH effect of a mixture of sodium hexametaphosphate (best additive)

Figure 9-9

Effect of Chemical Additives on Heavy Minerals and Solids in Froth

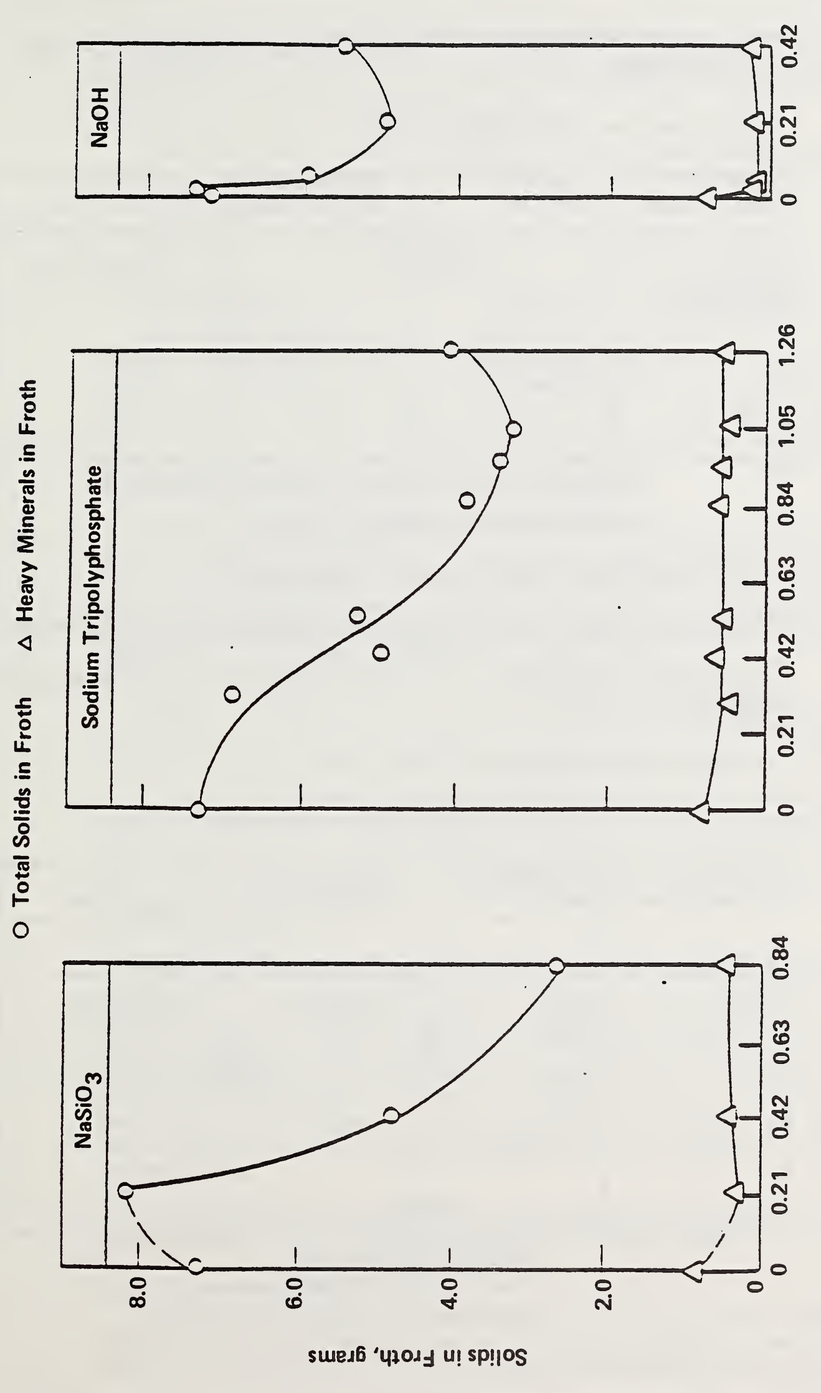


Table 9-4

Effect of Inorganic Additives on Solids Removal from Froth Separated with Aeration

Primary froth from core 33-14-2 top separated in bench unit (aeration) and containing 26% water and 13% solids*

(5 minutes mixing and 17 hours standing at 180°F)

Separation of Water Wet Solids	Small amount No Effect	Larger Amount Separated (<50%)	Separated (>50%)
Additive Only (wt% on Froth)	Na_2SiO_3(0.7) NaOH(0.6) $(NaPO_3)_6$ + NaOH (1.4) + (0.6) Additive + HCl(Dil)	Pyro-$Na_4P_2O_7$(1.5) Hexameta-$(NaPO_3)_6$(1.4)	Tripoly-$Na_5P_3O_{10}$(1.0)

-------(1) Decreasing amount of sludge in separated water-wet solids →
-------(2) Decreasing amount of water in oil phase →

* Some water and solids separated in transit and standing froth was rehomogenized prior to study.

Effect of Inorganic Additives on Solids Removal from Froth Separated without Aeration

Froth from Beaver Creek Bench #1 Tar Sand in CSAI Pilot Unit (No Aeration) containing 10.0% water and 3.2% solids*

(~15 minutes mixing and standing for 24 hours at 150°F)

------------------ Improvements over base case ------------------→

Separation of Water Wet Solids	Small Amount No Effect	Larger Amount Separated (<50%)	Separate (>50%)
Additive Only		$Na_5P_3O_{10}$ (T.P.P.)	
Varsol (s/o = 1.2) Pins Additive	NaOH Na_2CO_3 Na_2SiO_3 (1) 200 (2) GD (3) Anhydrous Na_3PO_4	$Na_4P_2O_7$(pyro) Dequest Phosphate "2006"	$Na_5P_3O_{10}$(TPP)

Decreasing amount of sludge
--------------- In water wet solids and ------------------→
Total amount of emulstion

* Some water and solids separated in transit.

with sodium hydroxide resulted in a poor separation. The use of slightly alkaline buffered solutions may provide a better technique for additive evaluation as well as a means of a plant control.

Beaver Creek froth formed without aeration and inorganic addition only, is best with polyphosphates. With solvent addition, the same general trend of inorganic agents was observed. It is interesting to note that Dequest phosphate 2006 appeared in this case to be between sodium tripolyphosphate and pyrophosphate in effectiveness.

These general trends parallel the addition of these inorganic agents in hot water flotation (Sections 6 and 7) as well as the order of phosphate effectiveness. The exception in this latter case is Dequest 2006.

The addition of the same amount (1 wt% on froth) of sodium tripolyphosphate to froth or froth diluted with Varsol results in separation of about the same amount of water-wet solids. Separation from solvent diluted froth is generally more rapid and slightly higher.

The emulsion settling effect can be attributed to the solvent dilution. The water-wet solids removal is attributed to the amount of sodium tripolyphosphate. The amount of solids removed appears to increase linearly with the amount of sodium tripolyphosphate added, accompanied by a linear decrease in emulsion volume. It is suspected that the water content of the total oil-solvent-emulsion phase also decreases substantially with increasing amounts of sodium tripolyphosphate. Water addition to the system results in flotation of the oil-solvent and emulsion phases, and aids the physical separation of water-wet solids.

Exploratory experiments on reducing froth to date have been most interesting and indicate promise. The idea of reduction was first proposed as a logical extension of our theoretical considerations. Its application to primary separation in the hot water flotation process proved difficult and the results were inconclusive. However, working the separated froth, the effect of reduction appears greatly enhanced probably due to the fact that the problem of complete separation has now been concentrated in the froth, i.e. oil-solid attachment.

The effect of hydroxylamine on a system of froth with solvent addition was the separation of a larger amount of clean water-wet solids. The oil-solvent/water interface was clear and only a very small amount of emulsion appeared to be present mainly in the oil-solvent phase.

Sodium borohydride gave even more significant results then hydroxylamine. Good removal (~50%) of water-wet solids (mainly sand) was obtained with solvent and sodium tripolyphosphate. A further amount of solids separated after treatment with sodium borohydride. They appeared water-wet and the darker colour of these solids was due to a predominance of black heavy minerals. Under the microscope these solids appeared similar to the total minerals originally inspected.

The action of the borohydride was to first redistribute the emulsion in the oil-solvent phase through the action of generated hydrogen bubbles. Second, as the reaction subsided, larger amounts of water-wet solids settled out into the water phase leaving a very clear oil-solvent/water interface. A single skin appeared to exist at the interface most probably due to the colloidal clay material, since the water phase showed little evidence of suspended solids. In some experiments, the water phase was distinctly green in colour, believed to be a precipitate of ferrous hydroxide, as it turned red (ferric hydroxide) with air bubbling. The effects found with reducing agents are being investigated and will be measured quantitatively when the technique has been defined.

It was concluded that membranes are oxidized products of naturally occurring surfactants that are associated with polyvalent ions and some ion exchanged clays.

9-2-4 Organic Additives

Various organic additives have been tested to explore the possibility of emulsion reduction. The criteria (#1) of separation of water-wet solids from the froth has been used. It should be noted that water reduction in the oil phase can result from removal of solids (and sludge) through

Table 9-5

Effect of Organic Additives on Solids Removal from Froth Separated without Aeration

Froth from Beaver Creek Bench #1 Tar Sand Separated in CSAI Pilot Plant Unit (No aeration but NaOH addition) containing 100% water and 3.2% solids

(~15 minutes mixing and standing for 24 hours at 150°F)

	------------------- Improvements over Base Case ------------------->		
Separation of Water Wet Solids	No Effect	Small Amount Separated (2%)	Larger Amount Separated (50%)
Additive Only	Carboxymethyl Cellulose Breaxite and Blends[1]	Sodium Stearate	
Varsol (s/o = 1.2) + Additive	Armac T Breaxite and Blends[1]	Sodium Dodecylbenzenesulphonate Disodiumethylenediaminetetraoctate	NOPO Chelate - Resin A
Varsol (s/o = 1.2) + Additive (0.1%) + Water (50%)	Aero Thiocarbanilide 130 Superfloc 16 Aerofloat 238 Aerodepressant 610 Adogen 170A Dow Froth 200	Sodium Stearate (solids in aqueous suspension) Pluronic F 68	Carboxymethylcellulose NOPO Chelate Resin A
As Above Plus $Na_5P_3O_{10}$ (T.P.P. = 1.0%)	Breaxite and Blends[1]	NOPO Chelate - Resin A	
Additive (0.1%) Varsol (s/o = 1.2) Sodium Tripolyphosphate (1.0%)	Hyamine 2389 Aerosol O.T. (V. Large emulsion volume) Ethylene Diamine	Sodium Oxalate Sodium Citrate Dow Antifoam B NOPO Chelate	
	Silicone L77 (finely dispersed emulsion and sludge)		
	HLB 2, 4, 8, 12 (V. Large Emulsion Volume)	HLB 14 (Large Emulsion Phase) HLB 6 (Small Emulsion Volume in Water Phase)	HLB[2] 10, 16 and 18 (Small Emulsion, Cloudy Yellow Water Phase)

(1) Breaxite Nos. 941, 2520, 7590 and 50/50 blends.
(2) Mixtures of spans and tweens.

solvent and inorganic addition. Thus it is very difficult to assess the ability of a particular organic additive to reduce the water in the oil phase.

A few comments are worthy of note on the summary of the exploratory experiments in Table 9-5.

- (1) A "NOPO" chelate-resin A, having properties to form chelates with heavy metals, resulted in large amounts of apparently water-wet solids separation. It was not quite as good as sodium tripolphosphate.
- (2) Carboxymethylcellulose addition improved separation especially with solvent addition. Carboxymethylcellulose is known for its protective colloid activity which increases zeta potential and presents flocculation.
- (3) Sodium stearate was not as good as carboxymethylcellulose, and the separated material was held in suspension in the water phase.
- (4) Significant differences were found with surfactants of different HLB (hydrophilic-lypophilic-balance). This was somewhat similar to the results of addition of these surfactants in hot water flotation but the effects were greatly enhanced in these froth upgrading studies. Again, surfactants with high HLB's of about 16-20 appeared to be the better additives.

The addition of Breaxit 941, by itself or in combination with solvent did not result in separation of more than small amounts of water-wet solids. When added with sodium tripolyphosphate or solvent and sodium tripolyphosphate combination even less water-wet solids appeared to separate than in the base case.

EFFECT OF BREAXIT 941 ADDITION

Breaxit, Wt% of Froth(1)						
Solvent, Vol/Vol of Oil	-	-	-0.1	0.1	1.2	1.2
Sodium Tripolyphosphate, Wt%	-	1.0	-	1.0	-	1.2
Emulsion Volume After Settling	N	N	S	S	L	L
Amount of Water-Wet Solids	N	S-M	N	S	N	S

(1) Similar results were obtained with Breaxits 2520, 7590 and 50/50 blends. Concentration was varied with no effect, e.g. A series with 941 up to 5%.

An optimum combination, appeared to have a very beneficial effect. This kind of effect has also been observed with other combinations of inorganic and organic agents, and this area of experimentation requires careful investigation.

9-2-5 Summary

The main conclusion of these froth upgrading studies is that large improvements in emulsion breaking and solids removal can be achieved by chemical addition. The general effects of additives studies are summarized below:

- *(a)* ***Solvent*** *is essential for high rates of separation, and emulsion settling. Solvent to oil ratios of 0.7 - 1.4 give good results at 150-180°F. Low boiling and high aromatic content solvents appear to be slightly better types of solvent.*
- *(b)* ***Water*** *aids the physical separation of water-wet solids. It also affords a sink for soluble salts, i.e. decreases ionic concentration.*
- *(c)* ***Inorganic Additives*** *effect good separation of water-wet solids (at least 50%) especially fine silica. Sodium polyphosphates were found to be the most effective and the order of effectiveness was hexametaphosphate > tripolyphosphate > dequest 2006 > pyrophosphate.*
- *(d)* ***Reducing Agents*** *show promise of removing solids not readily removed by sodium polyphosphate. The reaction is believed to be a reduction of ferric to ferrous iron.*
- *(e)* ***Organic Additives*** *show fairly significant effects. A number of organic chemicals have been tried and a few have been found which are worthy of note in ef-*

fecting solids removal. These are chelating resin A, carboxymethylcellulose, sodium stearate, and spans and tweens of intermediate (8-12) and particularly of high (14-20) HLB.

It has been found that an initial solvent separation to recover the bulk of the oil in an upper oil-solvent phase with a lower sludge phase for further treatment and separation is attractive. It is estimated that about 90% of the oil might be recovered in this first step. The lower sludge volume can then be treated with a minimum amount of chemicals, discussed above, to maximize recovery of oil or minimize solvent loss.

9-3 Agglomerate Upgrading

9-3-1 Solvent Dilution

A number of experiments on solvent dilution and settling of froth (from Hot Water Flotation) and agglomerate (from Sand Reduction) generated in the laboratory from Area B type tar sands were carried out.

Two basically different approaches were used in these small scale laboratory separations. First, the weighed feed was mixed with solvent (varsol) and separated by addition of the mixture to water. This has been termed solvent dilution. Second, the weighed feed was mixed with solvent and then decanted to recover the oil-solvent solution. This technique in some cases was repeated. Any sludge in the oil-solvent phase which settled out in 10 minutes was returned to the sludge. The remaining sludge, i.e. mixture of sand and water-oil-solvent was then separated by addition to water to generate further oil in solvent and emulsion.

In both techniques the phases were separated using a separator funnel to collect the oil-solvent phase, an emulsion phase, and a water solids phase containing some oil. These three phases were analyzed for solids, oil and water. Oil recoveries and composition of the oil phases were obtained. The general plot of oil recovery vs. solvent oil ratio is shown in Figure 9-10. It can be seen that a minimum solvent oil ratio of about 0.7 was required to affect a substantial separation of oil and solvent phase. Higher solvent oil ratios resulted in only slightly higher oil recoveries and slightly less emulsion forming. The oil loss to the water phase decreases with higher solvent-oil-ratios, as shown in Figure 9-11. The lower plot in this figure shows a cumulative composition of the total oil phase which includes the emulsion. It will be noted that a higher solvent-oil ratio gives more emulsified water although less emulsion is produced. These results are only preliminary.

It has been observed qualitatively that this approach to upgrading the froth can be substantially improved by using are anhydrous technique and utilizing pH control with preferentially sodium phosphates and silicates. Perhaps surfactants may also be used to reduce the emulsion problem. However, a very thorough systematic evaluation of these variables and also rate data on settling will have to be carried out.

Figure 9-10

Oil Recovery Decreases with Solvent to Oil Ratio

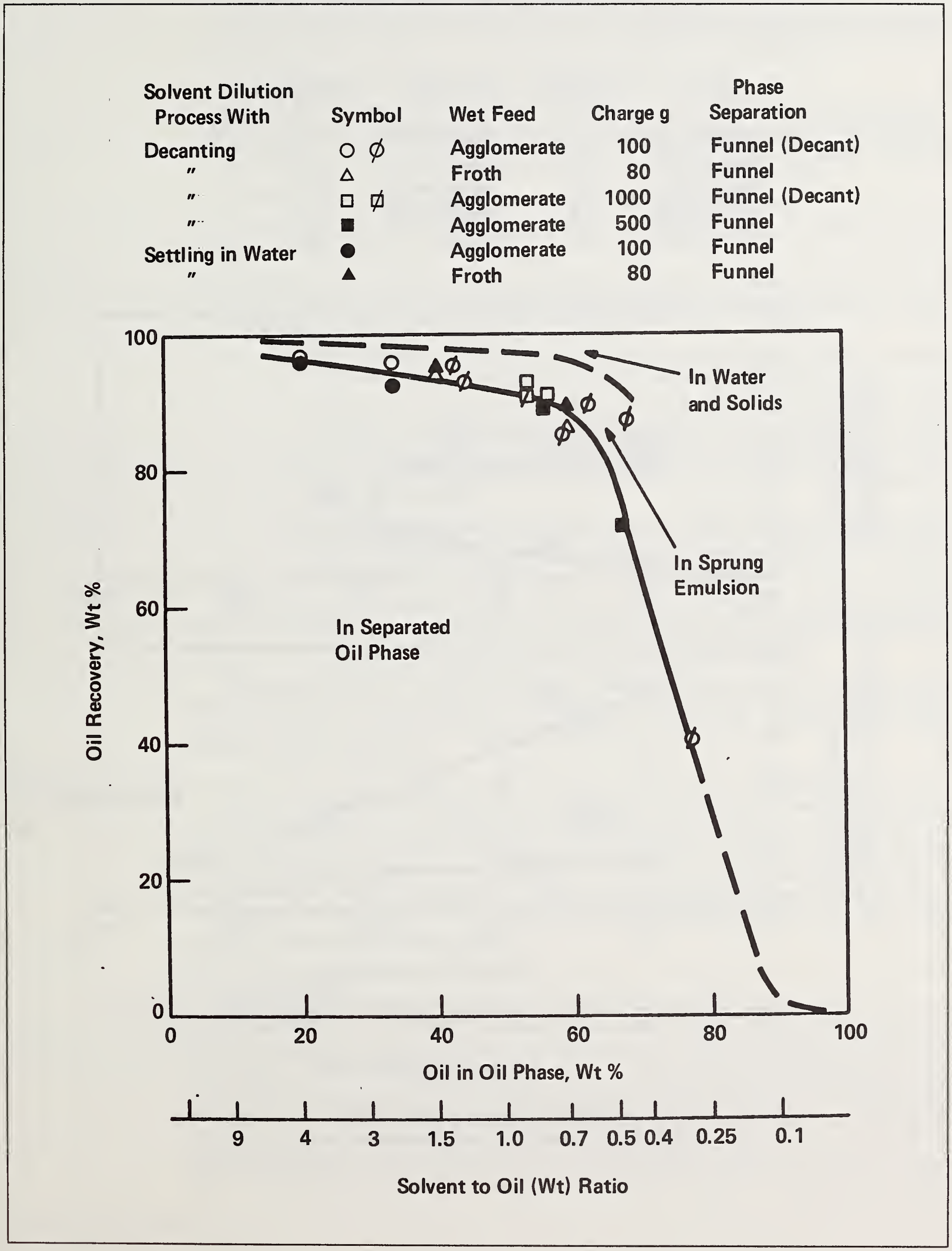
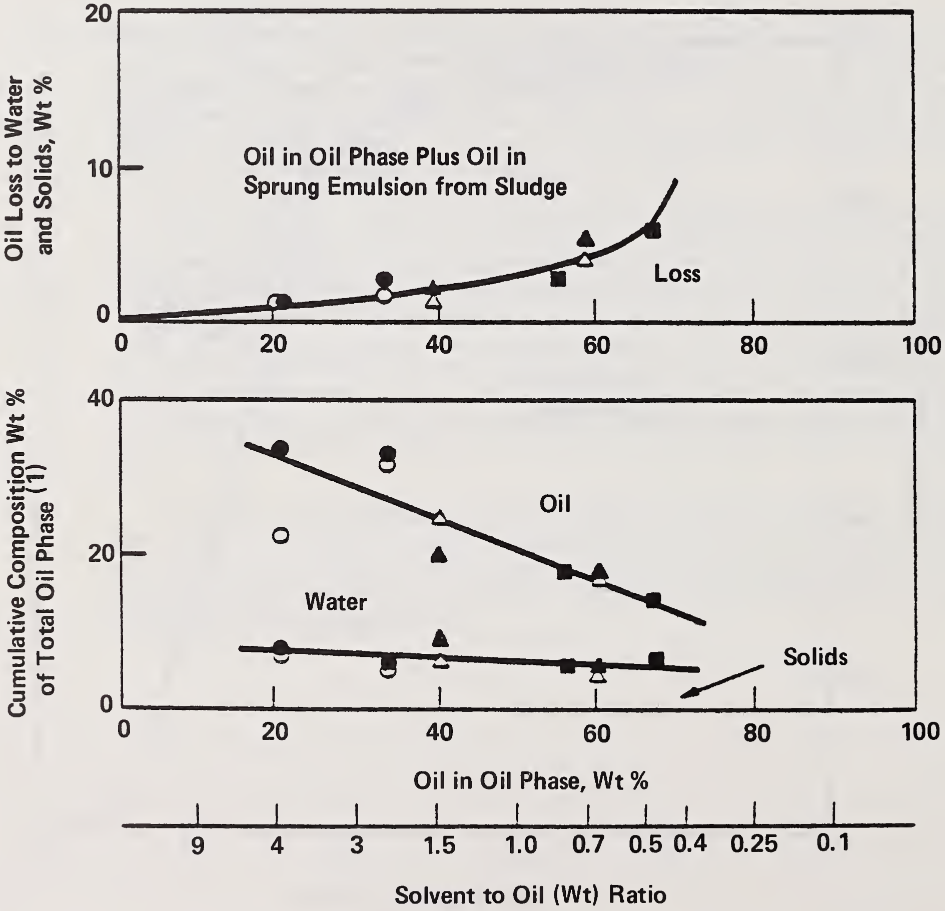


Figure 9-11

Water Content of Total Oil Phase Decreases with Solvent to Oil Ratio and Oil Loss to Water and Solids Increases

Process	Symbol	Wet Feed	Charge g
Anhydrous	○	Agglomerate	100
Anhydrous	△	Froth	80
Anhydrous	■	Agglomerate	500
Sol Dilution	●	Agglomerate	100
Sol Dilution	▲	Froth	80



Note (1): Sum of Oil Phase Plus Emulsion, Solvent Free Basis, from Funnel Separation

9-3-2 Other Solvents

Several qualitative studies have been carried out to evaluate the results of solvent type, pH additives and organic surfactants. The following observations have been made: -

- (1) Phenol, as a solvent, appears to increase the emulsion problem.
- (2) In general, the hydrocarbon solvents are very similar. However, the emulsion problem appears to be less with some types than others, although other conditions are complicating, e.g. temperature - viscosity. It has been observed that benzene is better than n-heptane, and varsol better than gas oil from the point of view of minimizing the emulsion problem.
- (3) Sodium salt addition pH control tends to reduce the emulsion problem.
- (4) Sodium tripolyphosphate and organic surfactants with HLB of 6-8 and 16-8 are most effective in reducing the emulsion problem.
- (5) Along the lines of forming a type of coacervate, a good quality froth was mixed with varsol, in one case, and with varsol and about 30% amyl alcohol in another. Pouring these mixtures into water, the following observations were made:
    - *(a) in the case of just the varsol, three phases formed, an upper oil and solvent, a lower water and solids, and a large emulsion intermediate layer.*
    - *(b) when amyl alcohol was added to the varsol, the separation resulted in only two phases, an upper oil and solvent and a lower water and solids. It is probably that the upper oil layer contained the emulsion in a dispersed form by the action of the alcohol which partitions between the two phases. However, clean separation could be effected.*
    - *(c)(b) was repeated with a poor quality froth. Again, a big improvement was obtained, but only about 75% of the emulsion went into the oil phase with amyl alcohol addition.*

In conclusion, it is believed that the skins or membranes are similar to those stabilizing emulsions in solvent dilution and settling, i.e. polyvalent salts of the anionic surfactants, the polyvalent ion being either free or adsorbed on a clay mineral or silica particle.

The approach should be to break those salts forming sodium soaps and free particles. This has been found to be best accomplished with sodium phosphates and silicates. The emulsion problem may be still further improved by the addition or organic surfactants, HLB 6-8 or 16-18, and alcohol. (See Appendix 6)

9-4 Membranes

The completeness of solids separation is determined by the degree of water wettability that is mostly high due to the normal hydrophilic nature of the solids and can be enhanced by addition of certain inorganic chemicals. The main practical problem in making the separation process work is the transfer of solids across resistant skin emulsions or membranes that accumulate at the interface. To overcome the resistance, force such as centrifuging or mechanical agitation has to be applied to effect solids transfer. The nature of the membranes and the transfer force needed to effect separation was therefore studied.

9-4-1 Occurrence

Membranes have been found to occur in all oil sands studies. Even good quality Area B exhibit appreciable amounts. Although not enough quantitative data was obtained, it appeared that more membranes per percent oil content occurred in poorer quality oil sands. Isolation of these membranes was achieved by concentrating them at a water-oil interface by repeated solvent dilutions and partial removal of the settled upper solvent/oil layer. This process was repeated until the membranes were observable at the interface, and could also be removed in a solvent phase. Membrane occurrence was estimated from some of these isolation studies to be <0.2 wt% on oil. Although membranes appear voluminous. However, the solids content (ash) varied from essentially 0 to 85%, that can account for a large amount of the total weight of membranes recovered.

9-4-2 Behaviour

The apparent viscosity of the membranes increases with solids content. At low solids content the films are resilient or rubber-like, and when broken reform again very rapidly. The higher the solids content of the membranes, the lower the rate of reforming, if at all, and the more rigid the film structure. This behavior is like a thick coherent laminar film with increasing rigidity depending on the degree of association with metal ions and solids.

Membranes however can be physically broken up and dispersed. Zeta potential measurements of both types of dispersed membranes in water were measured to be negatively charged at ~20m indicating a fairly stable dispersion, supports the observation.

Membranes exhibit a strong tendency to separate from an oil phase and accumulate at the oil-water interface. In contact with water, they exhibit a very low solubility as measured by UV fluorescence. These observations indicate an interfacial character having both hydro and lypophobic components. The main problem in separation of water-wet solids from solvent diluted oil phases is that the membranes accumulated at the interface impedes the passage of the solids until eventually enough weight of solids will burst through the interface with occluded solvent/oil. This results in large losses. A satisfactory solution to this problem using both mechanical and chemical energies could greatly improve separation by solvent dilution and hence the economic attractiveness of this process approach.

Membranes are stable under both mild acid and mild alkali conditions. High <11 and lower <3 pH's, however start to cause disruption of the membrane structure, e.g. Iron is readily detected using sodium thiocyanate in the aqueous phase. Membranes are dispersed in water more by sodium tripolyphosphate than any other chemical studied. Silicates sometimes showed a similar affect. Hence, the polyvalent metalious associated with these naturally occurring surfactants appear emission spectra also indicate other possibilities such as manganese and aluminum.

9-4-3 Organic Component

After membrane isolation in a solvent, e.g. toluene that was mostly used, the solvent was removed by evaporation under nitrogen, and then the organic portions of the membranes was dissolved in either chloroform or pyridine. Any solids were separated by centrifuging. Evaporation of the solvent phase enable the organic surfactant to be obtained in a fairly fine state. In some cases, acid treated membranes were treated with chloroform and centrifuged. The results appeared to be the same.

When purified, the organic component appears to be colourless-yellow and of high molecular weight. It also exhibits a somewhat waxy character. When impure, it is black and resinous, although this observation may have resulted from oxidation.

Only extremely small quantities of organic material were available after membrane isolation, solids separation, and purification of the surfactants. Thus, infrared analyses were used to obtain preliminary identifications. Very much larger scale separations will have to be carried out to obtain enough purified material to obtain detailed elemental and hydrocarbon analyses, for a better definition.

The infrared spectra shows characteristics peaks for carbonyl ester and acidic groups. They hydrocarbon portion, together with some supporting NMR data, indicates a more aliphatic character. This is also supported by the waxiness of the isolated material.

Hence, it was tentatively concluded from several of these repeated operations on different samples, that one of the organic components of membranes is an aliphatic type carboxylic acid, probably of high molecular weight as well as "oxidized". It appears to have reacted with polyvalent ion either per se or associated with solid surfaces to form stable carboxylates.

These bonds have to be either hydrolyzed by strong acid or bases or reacted with selective chemicals such as sodium tripolyphosphate that can also sequester the polyvalent ion while forming the sodium salt of the acids.

9-4-4 Inorganic Components

The centrifuged solids from separation of the organic material were washed with pyridine and then with chloroform and dried under nitrogen. The solids were separated using tetrabromoethane into light and heavy minerals and both fractions were inspected using microscopic techniques.

The solids in the membranes that are low in solids <5% Ash) are essentially very fine <5% clay minerals and iron compounds. The ratio of the predominant metals present Si:Fe:Al was found to be 4:3:1 by emission spectra. This ratio is typical of solids (ash) from the total oil-solvent phase.

The solids in the membranes that were high in solids >50% contained more than half, i.e. 21-42%, heavy minerals.These minerals appeared to be mainly nonopaques with gross surface deposits of iron; and titanium minerals, such as leucoxene and ilmenite in the lower size range of up to 40 micron. The light minerals were a mixture of fine silica, clay minerals and iron compounds of smaller size range than the heavy minerals. However, all the minerals observed under the microscope are typical of the mica suite, but small in particle size.

However, the high concentration of heavy minerals found indicate a great number of stronger positive surface sites for the formation of stable carboxylates, than those that occur on higher minerals such as clay. Heavy mineral concentration in froth, however, has been observed before.

9-4-5 Summary

It appears that the main organic component of membranes are aliphatic type carboxylic acids, see also Section 2. These occur, in variable association with both polyvalent ions, fine minerals, and especially heavy minerals, as carboxylates. These two interconvertible polar groups probably broaden the membrane problem in solvent dilution in that (a) the more mobile free acid form the reform resilient skins (coherent laminar films) impeding the transfer of solids across the solvent/oil-water interface, while (b) the more rigid carboxylate skins accumulate at the interface compounding the problem of separation into clean phases. A summary of the several aspects of substances is given in Table 9-6.

9-5 Separation Techniques

The several studies (already discussed) employing solvent dilution were carried out in attempting to upgrade froth from hot water separation of Mildred Lake Oil Sands. These studies were mainly concerned with the effect of near and chemicals on settling with and without solvent dilution. Membranes were identified as a key reserved area. Further, the heart of the problem of solvent dilution is really one in which tough emulsion skins, which accumulate at the oil-water interface present a resistance to the transfer of particles across the interface. After settling the bulk of the solids in the oil-solvent phase to the interface, the weight frequently resulted in large "sludge" volumes disengaging into the water phase with consequential high oil losses.

Additional studies were therefore carried out to find techniques of overcoming membrane resistance in separation. Mechanical agitation at the interface ultrasonics, electrostatics, and centrifuging separation using a fresh froth from pilot plant separations on Beaver River Oil Sands. This froth was found to separate in solvent dilution more readily than previous Mildred Lake forth obtained from the Bench Unit.

9-5-1 Centrifuging

Centrifuging is the best method of removing most of the solids from the oil phase. In this particular case, it removed about 85% which was twice as much as that obtained in settling. The solids that separated occurred mainly in the initial stages of treatment, i.e. less than 30 minutes.

SOLIDS IN SEPARATED OIL

Separation Time, Hours	5	1	1/2
No. of Experiments	33	6	7
Average Solids, Wt% on Oil Only	1.7	1.8	1.6

Table 9-6

Membranes

1. **Organic Components**
    1. Aliphatic carboxylates in high solids membranes.
    2. Aliphatic carboxylic acids in low solids membranes.
    3. Yellow to white, resinous materials when pure. Dark brown when impure with frequent separation of waxy micro crystals.

2. **Solids Components**
    1. Heavy minerals (~35%) and light minerals (~65%) having a ratio of Si:Al:Fe of 4:1:3 occur in membranes that are high in solids content.
    2. Very fine (<5μ) clay minerals and iron compounds having a ratio of Si:Al:Fe of 2:1:1 occur in membranes that are low in solids content.

3. **Physical Properties**
    1. Coherent interfacial films demonstrating both lypophobic and hydrophobic character.
    2. Solids and organic components are variables, therefore, properties vary:
        (a) High solids* - rigid films, high viscosity, etc.
        (b) Low solids - resilient films that reform, stabilize emulsified water, etc.
    3. Can be mechanically broken. Dispersions exhibit a zeta potential of -20 mv.

4. **Chemical Properties**
    1. Stable under mild acid and alkaline conditions.
    2. Polyphosphates are best dispersants of high solids membranes.
    3. Very low solubility (U.V. fluorescence), which increases with pH.

5. **Question to be answered**
    1. What is the interconvertibility of the organic components i.e. rate of ionization as function of pH, stability of salts, etc?

* Also polyvalent ions, e.g. Fe.

A study of solids removal by centrifuging as a function of both relative centrifugal force and separation time was carried out with Beaver River for the Run #109. In general, increasing centrifuging time at a constant relative centrifugal forces does not appear to effect any significant change in the equilibrium obtained after about 1 minute, Figure 9-12. The scatter in the data is attributed to sampling inconsistencies. However, solids and water removal from the oil phase decrease to low levels of about 0.1 to 0.7% respectively after about 20 minutes at 200G. Slightly lower contamination levels are achieved in about 13 minutes at 1800G.

The effect of the relative centrifugal force on solids removal, and contaminants remaining in the oil phase is also shown in Figure 9-12 for a three minute operation. The bulk of the separation is achieved at relative centrifugal forces of greater than 200G in this time. It should be noted that the solids content of the oil phase has been determined by ash analyses, and hence will reflect inherent solids such as Fe, Ni, V etc in the oil. Thus these values refer to the total solids.

With both the types of Beaver River froth used in these studies, a maximum of about 90% solids removal was attainable. The unremoved solids, which are apparently associated entirely with the oil, with separate after extended standing. This separation process is very slow. However, these solids will separate to the interface as gray-brown solid type membranes which can now separate readily into the water phase.

Centrifuging as a process for either upgrading the total froth or recovering oil from an oil-solid-water emulsion is quite the most positive method of separation and results in an oil phase of very much lower solids contamination than the maximum level required by oil upgrading processes, such as coking. Solvent-dilution settling can give rapid removal of large solids, with initial solids pre-conditioning a critical variable. Further studies were undertaken to firm up the possibility of an integrated, dilution-settling with emulsion-centrifuging approach to separation. The criterion of the process would be to reduce the contaminants to acceptable levels for direct use of subsequent conventional oil upgrading processes.

This method has been found to be the best method of reducing solids in froth. This is accomplished with oil losses of less than 1%, and the resulting oil phase containing less than 0.5% solids and 1% water, based on oil at fairly mild relative centrifugal forces of about 200G. Solids removal of 85-90% occur in about 1 minute. Further separation is very slow, but will take place to almost completion, i.e. 0.1% solids on oil. Although centrifuging is the most effective method, however, high cost of equipment required that minimizing the feed volume might effect savings.

9-5-2 Ultrasonics

Three* basic types of ultrasonic equipment were evaluated at frequencies from 60 cps to 100 KC kilocycles/second. In general high frequencies did not assist separation, however, low frequencies, even up to 10,000 cps did not bring about a small effect. This effect is mainly the emulsification of oil in the water phase. The latter turns light brown. However, the initial IR patterns of separated emulsified oil in water became very quickly similar to that of oil itself in the initial stages of treatment.

It was therefore concluded that ultrasonics was not an attractive approach as even settling itself, based primarily on the oil losses incurred in separation of bulk-sludge, and emulsification of oil in the water phase. This latter effect is greatly increased in the presence of added chemicals.

An example of ultrasonic separation at very low frequencies of 60 cps is shown in Table 9-7 and Figure 9-13. The results show that this method is not very effective.

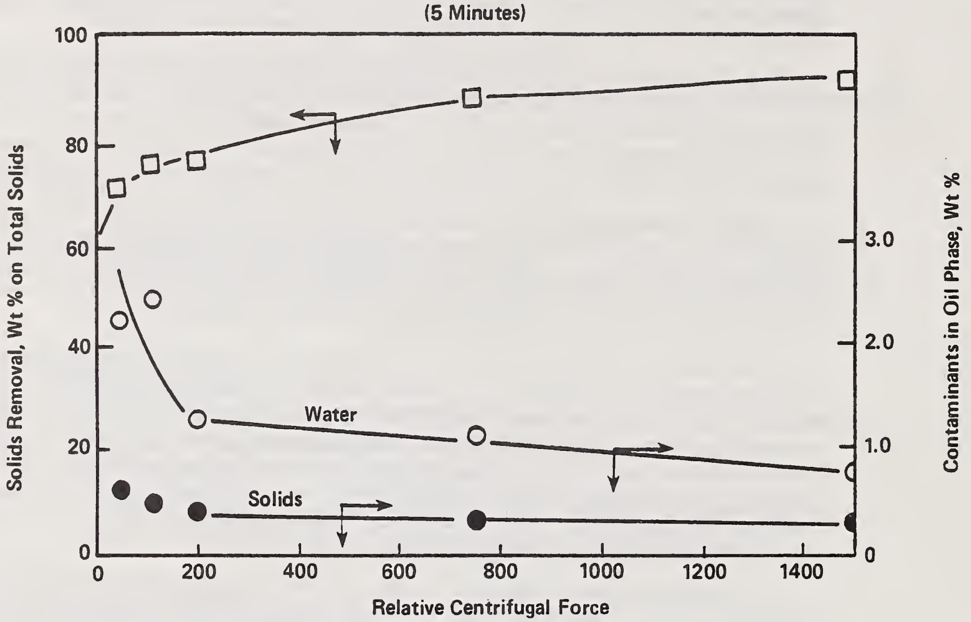
---

*The Autosonic Model PA-3001 Output - 60 cycles

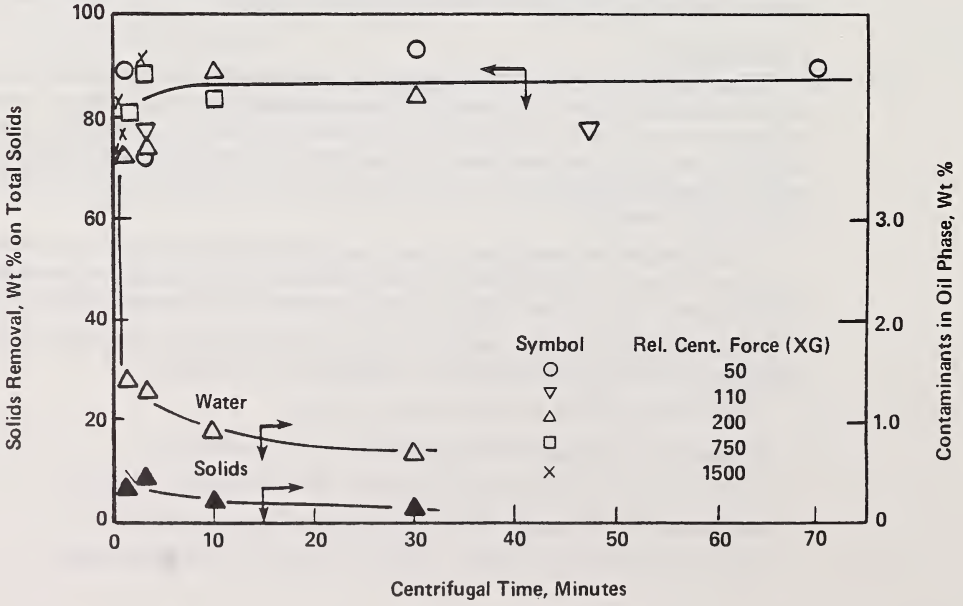
- Raytheon Sonic Oscillator Model DF101 Output - 250 Watts 10 KC
- Hypersonic Generator Model BU-204 Output - 250 Watts 100 KC - 1000 KC
- High Voltage D.C. Generator 13,600 V D.C. at 25 μa 1.6 ma at 250 V D.C.
- Sorenson Unit Model 1061 Output - 10,000 V, 10 ma Use - 60% Power Input

Figure 9-12

Preliminary Data on Solids Removal and Contaminants in Oil Phase vs Centrifugal Force



PRELIMINARY DATA ON SOLIDS REMOVAL AND CONTAMINANTS IN OIL PHASE VS CENTRIFUGING AND RELATIVE CENTRIFUGAL FORCE



9-5-3 Electrostatics

Previous studies in electrostatics showed little effect on separation of this technique over just settling. The conclusion was that the voltage drop across the oil-water interface was short-circuited through the interfacial emulsion. These studies, however, were carried out with poor quality froth from the Bench unit with which emulsion problem were more predominant. Improved quality froths from the lower-energy, continuous pilot plant operations, gave a more reduced emulsion volume at the interface. This emulsion was more compact and in the form of membranes or coherent films at the interface.

It was, therefore, thought that electrostatics may be more applicable to this type of emulsion, as others had claimed success with this method, in general deulsification. Experiments were carried out in which the voltage was varied up to 10,000 volts. As before, the current increased with the amount of water in the system and various techniques, e.g. using fluoro-chemicals, had to be used to maintain high voltages. In all the experiments carried out, no visual change with electrostatics over settling was observed.

The only success of this technique was in effecting agglomeration of the oil from a very stable emulsion in water caused by ultrasonic treatment of a system of oil-solvent in contact with water. Again it was concluded that electrostatics is not a good method of froth upgrading. (See Appendix 6)

9-5-4 Mechanical

Effectively, three methods of energy input at the interface were studied. These were: (a) stirrers, (b) jiggers, and (c) vibrators. Comparisons were made in the apparatus described in the Appendix, as well as, in larger similar pieces of equipment.

An example of these operations are summarized in Table 9-7. These comparisons showed that basically similar results were obtained in the presence of all these types of energy input. However, stirring and jigging did not effectively break up the membranes, and oil association with the elements at the interface was common. Any rupturing of the membranes were quickly reformed by their nature to coalesce into a coherent film. Many varieties of paddles, sizes, speeds, and amplitudes were tried, but with little success.

A reference using ultrasonics at 60 cps is also compared with stirring and jigging operations in Table 9-7. This operation was typical of those found for just settling, except for in the input energy from ultrasonics promoting more bulk-sludge separations and hence incurred larger oil losses. It was found that just settling on a small scale could result in very erratic results caused by indiscriminant disengaging of sludge from the oil-solvent interface, with incurred oil loss.

The best mechanical method devised to improve the separation is to use a 16 or larger U.S. mesh, flat or corrugated, screen horizontally in the interface.

9-5-5 Vibrating Screen

Vibrating appeared to be the most consistent and effective method of breaking up the membranes. The best technique involved a screen of about 16 U.S. mesh placed in the interface and vibrated at about 60 cps that cause a pumping action to occur in the immediate vicinity of the interfacial membranes. Increasing the input energy increased the amplitude of the vibrations and caused a larger emulsified zone to occur at the interface. The technique appeared to work best at the lowest amplitudes studied, of about 1 mm. The action of the vibrator was to break the membranes into very fine pieces together with a circulatory motion, in which the membranes floated back to the interface. At the lowest amplitudes the emulsified zone was something less than about 1 cm. No fouling of the element was found in any equipment. This important point, indicated that this mechanical device might be used for indefinite periods, and this has been indeed verified to a small extent in subsequent glassware separation. The actual separation of solids was slightly better than that for just settling. However, in this case as in all subsequent cases, the oil loss together with solids separating to the water phase was substantially minimized. The main conclusions of these studies are summarized:

Table 9-7

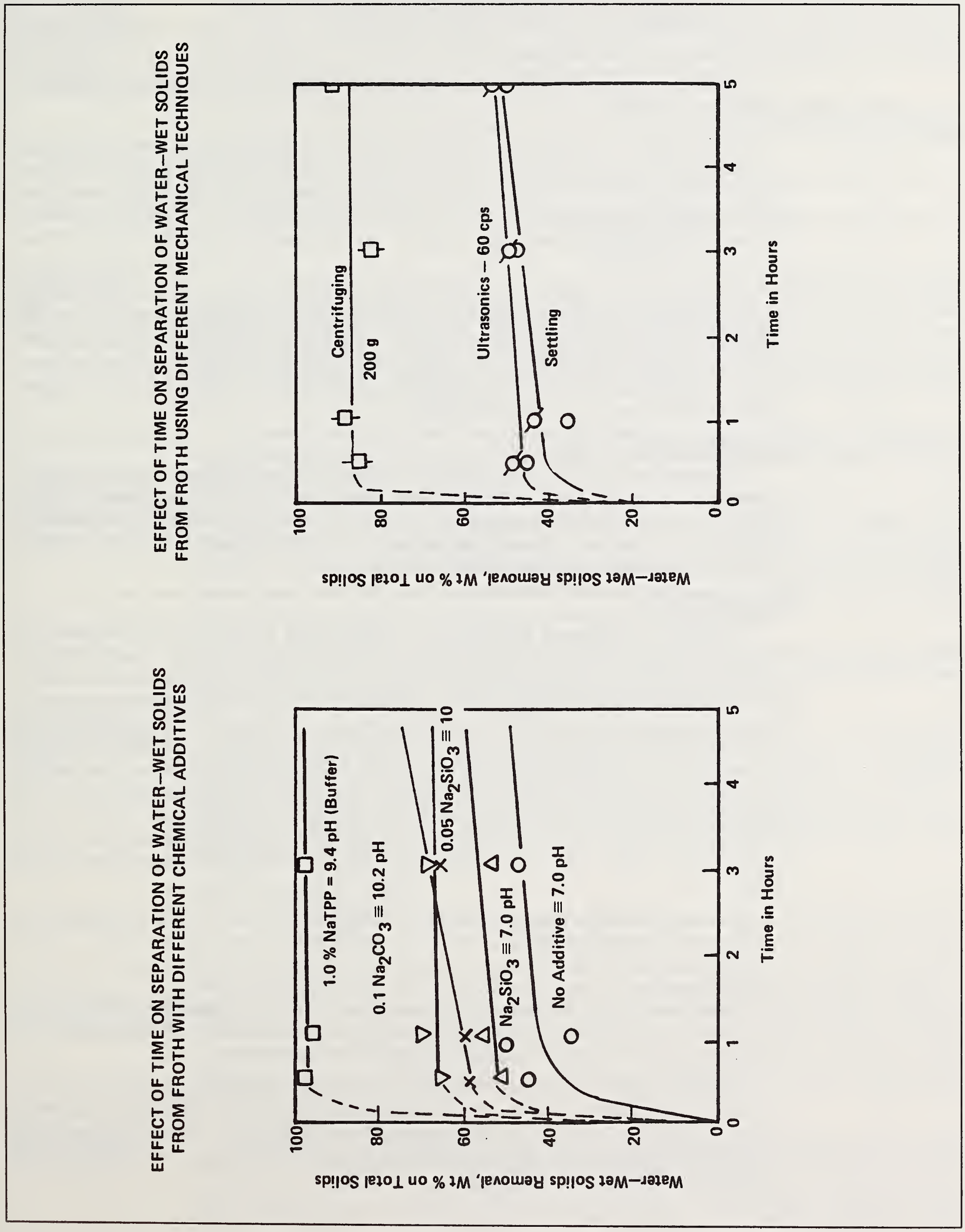
Comparison of Methods of Oil -Water Interfacial Agitation (3 Hours Operation at 165 °F, 1:1 Good Quality Beaver River Froth to Toluente Wt Ratio)

Type of Interfacial Agitation	**None**	**Stirring**[1]	**Jigging**[2]	**Vibrating**[2]	**Ultrasonics**
Rate of Agitation (Amplitude)	0	1000 rpm	0.8 cps (1/2")	60 cps	60 cps
Results, Wt%					
Oil Phase:					
Solids	2.3	2.0	2.0	2.2	1.7
Water	1.1	1.0	0.85	0.7	1.1
Solids Release	14	23	24	27	35
Oil Loss	0.5	0.3	0.3	0.05	0.4
Observations					
Effect on Skins	None Hanging	- Breaking and Reforming - of Large Skins		Broken Into Fine Pieces	None
Skin Removal Skins Sank	As Sludge to Interface	------ Some Large ------ Sludge		Circulates Back	As Bulk
Effect on Mechanical Element	--	--------- Fouling ----------		No Fouling	--
Visual Rating of Sep'n of Water Wet Solids	Poor	--------- Better ------------		Good	Poor Because of Sludge

(1) 3 vertical blades and 6 blades on a disc were equivalent and the main types of stirres used.
(2) The element used in these tests was a 16 mesh, 1-1/2" circular screen. Only the edges in the case of jigging was effective in breaking skins because of fouling.
(3) An ultrasonic oil bath was used to convey the oscillation - frequency to the immersed apparatus.

Figure 9-13

Effect of Time on Separation of Water-Wet Solids from Froth with Different Chemical Additives



- *(a) Vibrating was found to be the most positive mechanical method of breaking up the interfacial membrane films.*
- *(b) Vibrating was better than just settling alone in that:*

(i) an equivalent or better solids removal is obtained,

(ii) lower oil losses are incurred, and

(iii) more consistent performance, avoiding indiscriminant oil loss due to sludge separation with just settling alone.

In application on a large scale, some holes may have to be cut into the screen to facilitate recirculation. The end effect is an oil in water interfacial emulsion layer which can be withdrawn as the middling stream and treated separately or in conjunction with any sludge stream from mixing. Dielectric probes could be used to maintain a fixed location of the emulsion zone and to control withdrawal of minimum sludge centrally from the vibration zone, rather than from an outlet in the side vessel.

In small scale experiments the rod transmitting the vibrations to the screen at the interface passed through the oil phase. It would be better on a large scale to form an upper quiescent zone for efficient settling in the oil-solvent layer and transmit the vibration to the screen either through the water phase or from above using a sleeve around the vibrating rod. Feed introduction at or near the oil-water interface would minimize settling distance and minimize the upper quiescent settling zone in the oil-solvent phase.

9-5-6 Comparison of Methods

A comparison was carried out between settling with and without chemical addition, ultrasonics, electrostatics, and centrifuging. This comparison involved the duplication of experiments for different times of separation, e.g. 0.5, 1, 3, and 5 hours of separation. The individual methods will be discussed separately below. The results plotted in Figure 9-13 shows centrifuging to be the best method without chemical addition.

9-5-7 Chemicals

The effect of addition of sodium salts on settling using a vibrating screen separation of water-wet solids as a function of time is shown. In all cases the pH was either neutral or slightly alkaline. With all additions of sodium salts, improvements were effected. The results showed almost horizontal lines, as a function of time, indicating that most of the solids that were going to separate, separated in less than 30 minutes. These results show that solids pre-conditioning with chemicals in mixing is an operative factor. It is not possible from this data to distinguish between the functions of pH and reaction of the anion, but the latter does appear to have a significant effect. With this particular Beaver River froth and 1% sodiumtripolyphosphate, about 97% of the solids were removed. This unusual success has not been found to be general occurrence with different types of froth. Emission spectrograph data on ashes from experiments with and without polyphosphate addition show heavy minerals and iron to be almost eliminated from the froth solids.

The best result with addition of sodium tripolyphosphate was superior to separation by centrifuging, compare Figure 9-13.

9-5-8 Summary

Centrifuging is the most positive physical method of effecting separation of contaminants from solvents diluted froth generated by hot water separation. Ultrasonic and electrostatics were ineffective methods of improving dilution-settling with out additives.

Addition of alkali sodium salts were found to accelerate the rate of separation and to effect recovery improvements in dilution settling using a vibrating screen to facilitate solids transfer across the interface. Sodium tripolyphosphate (0.25 wt%) with Beaver River froth gave ~98% recovery that was superior to that of centrifuging alone. The contaminants remaining in the oil phase were <4% solids and 0.3% water.

These promising small scale results need confirmation in large scale continuous demonstrations before being considered a viable competitive approach to centrifuging.

9-6 A Continuous Solvent Dilution Process

The same apparatus and basic technique were used to explore this potential process in short runs. Standard condition were arbitrary, convenient, and mild, that gave consistent operation, but not necessarily the best results. The main standard conditions that will be discussed in greater detail in this section, are 155°F and Xylene solvent to froth weight ratio of 1.0.

The study objective was to explore the variable of temperature, pH, chemical effects, concentrations, mechanical energy input etc. to derive a more optimized set of conditions for further demonstration.

9-6-1 General Conditions

Using the standard set of conditions, a short separation study of the effect of temperature on the rate of solids transfer across the interface was undertaken.

(a) Separation Time

An example of solids separation as a function of time is shown in Figure 9-14. It will be noted that the initial separation of solids occurring in less than 10 minutes is more critical than subsequent separation with time. Further, this rate of separation decreased with solids removed as approximately a linear function of the logarithm of separation time. Solids separation appeared to be essentially independent of temperature, although oil loss did appear to increase slightly with increasing temperature.

The results with good quality froth were not very encouraging. Microscopic inspection of the separated solids showed the solids that separated to be mostly large silica with some heavy minerals and appeared "effective water-wet".

(b) Particle Size

In order to evaluate the apparatus and technique, to verify at what rate solids would separate, a series of calibration experiments were carried out. In this study a synthetic system was used, which contained 6% of water-wet silica spheres of different size ranges in water-solid free oil phase containing a 1:1 Xylene to oil ratio. It was found that about 95% of the silica spheres that were greater than 10 microns separated in less than 10 minutes.

As about 80% of the total solids in the froth are greater than 10 microns, the poor results shown in Figure 9-14, support an alternate mechanism to Stokes Law as operative in dilution settling separation, preventing the transfer of solids across the oil-water interface.

(c) Solvent to Oil Ratio

In most of these experiments a 1:1 froth to solvent weight ratio was used, or a 1.3:1 solvent to oil ratio. Previous studies had shown that solvent to oil ratios of 0.7-1.5:1 did not appreciably affect initial separation, but only the ultimate quality of the oil phase in a given settling time, i.e. Stokes Law operative and higher oil losses is incurred at lower solvent/oil ratios. Less contamination in the oil phase as a function of solvent to oil ratio was indicated principally from relatively lower oil phase viscosities.

9-6-2 Chemical Addition

Chemical addition in some cases can give significant process changes, although the reasons are not fully understood. However, chemical addition does not buy any means eliminate membrane-emulsion problems, and can even cause further emulsification of water in the oil phase. Some froths are more susceptible to chemical addition than others. Chemical addition is solid form to either the froth or froth-solvent mixture has not proved satisfactory as the chemical becomes oil-wet and, hence, ineffective. Chemical solution addition in either mixing with froth, or simultaneously with solvent addition, or with the froth-solvent mixture, all appear equally satisfactory methods on a small scale. The simultaneous addition with solvent technique was adopted as standard procedure.

(a) Carbonates and Silicates

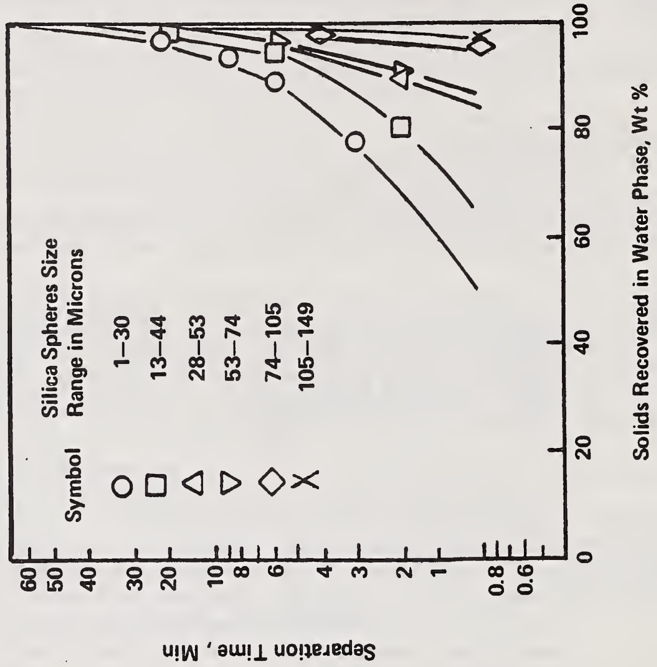
An example of increasing the concentration of sodium-carbonate in mixing on the solids removal is shown in Figure 9-15. The slope of the linear plot decreased with addition, indicating a slight improvement in the rate of separation. The addition of sodium silicate is also shown. Adjusting the pH of the water phase with a very small quantity of this additive resulted in almost

Figure 9-14

Solids Separation Independant of Temperature

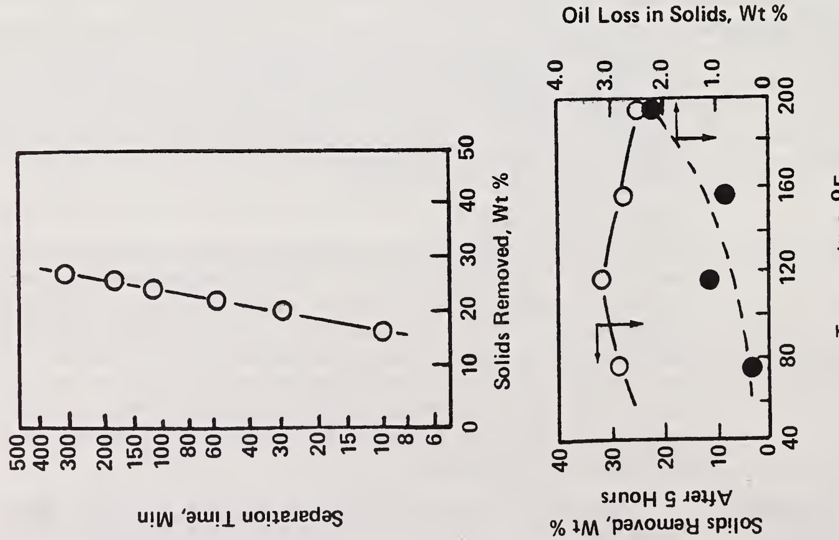
SEPARATION OF DIFFERENT SIZED SILICA SPHERES FROM A 1:1 OIL–SOLVENT PHASE

(155 °F, Water–Wet Solid Conc. – 6 % on Oil Phase)



SOLIDS SEPARATION IS INDEPENDANT OF TEMPERATURE

(Standardized Conditions)



significant improvements in the initial separation of solids. This indicates that ions in the water phase may also disperse the membrane sacs. Several other simple inorganic chemicals including sodium polyphosphate were also investigated. The results are summarized in the Appendix. In general the results are best interpreted in terms of pH.

(b) Effect of pH

The results of chemical additives with good quality froth under mild standard conditions have been plotted in Figure 9-16. The results in general were poor, by significant improvements were found at an optimum pH of about 9.5.

Excess alkaline chemicals caused poorer separation. This can be a problem when using significant amounts of chemicals in concentrated solution additions to a mixture of froth and solvent mixing. This concentration effect can also be interpreted as an adverse pH effect in mixing. The order of chemical effectiveness found to minimize water in the froth and maximize water-wet solids removal is $Na_5P_3O_{10} > Na_2 SiO_3 > Na_2CO_3 > NaOH$.

Acid conditions did not cause a significant deterioration of the separation, as is found in hot water flotation using Beaver River Froth (Run #109). In terms of solid separation the results are good and confirm that acid conditions do not appear to adversely affect separation as in hot water flotation. In fact, a slight improvement is evident at pH's less than 3, where appreciable irons was found in the water phase. This tends to support the theory that surfactants and membranes are joined to solids in the emulsions by bridging polyvalent metal ions, such as ferric iron. It will be also noted from Figure 9-16 that a small maximum is also evident at about 10 pH. However, the pH of the water phase does not appear to be a variable and control point. This stream should be monitored and adjustment made by chemical addition to maintain ~9±1 pH.

(c) Effect of Concentration

The effects of sodium polyphosphate concentration on separation and of different types of Beaver River froths are shown in Figure 9-17. An optimum at pH's very approximately near 9-10, was indicated at concentrations of about 0.3 wt% on all types of froth. It appeared that good quality and Bench #1 froths may have been more susceptible to chemical addition than medium quality froth. The latter froth and Beaver River froth Run #109 gave about 60% solids removal.

High values were also obtained with spot samples from the bottom of sample cans, which were investigated to verify that water-wet solids settled on standing from froth. In these cases about 85% solids removal was achieved. It should be noted that Bench #1 Beaver River froth contained more heavy minerals, which separated on standing. Whereas the solids content of Beaver River froth Run #109 showed only about 20% increase in total solids content. All other series of experiments were carried out with sampling from homogenized batches of froths.

(d) Effect of Breaxit Addition

The emulsification of oil in water found with pyrophosphate required that *no vibration* be carried out at the interface, using this additive. Thus, using only a settling system, combinations of pyrophosphate and different Breaxits were briefly studied. Breaxit sample No. 941 gave a 7% increase in solids removal over the settling. Other Breaxit samples No. 7590 and No. 2520 gave identical results to the settling. A mixture of tripolyphosphate and No. 2520 gave almost twice as much solids removal than the corresponding experiment with pyrophosphate; the reason is unknown, but attributed to an anion effect. This tends to substantiate previous finding that tripolyphosphate is the better phosphate. The effect of Breaxit addition may be taken as having little effect on solids removal, but the water content of the oil phase was substantially reduced to less than 2.0% oil, compared to 6.0% with settling and chemicals.

(e) Miscellaneous Separations

Many experiments have been conducted to develop the laboratory separation technique, as well as to evaluate factors such as air, H_2O_2, calcium salts, etc. The results of these latter experiments are recorded in the Appendix

9-6-3 Optimum Energy in Mixing

In general, the principle, of "gentle mixing" advocated in flotation also applies in froth upgrading with solvent-dilution. Mixing intensity is somewhat critical in that high speeds <5000 rpm cause very severe and stable emulsification of water and solids in oil, particularly with chemical separation of water-wet solids and exhibit higher oil losses. Intensity is also function of mixer design and, as sludge sinks readily in an oil-solvent phase, horizontal mixers, e.g. inter-

Figure 9-15

Effect of Sodium Carbonate and Silicate Addition on Water-Wet Solids Removal from Good Quality Froth by Solvent Dilution (Standardized Conditions)

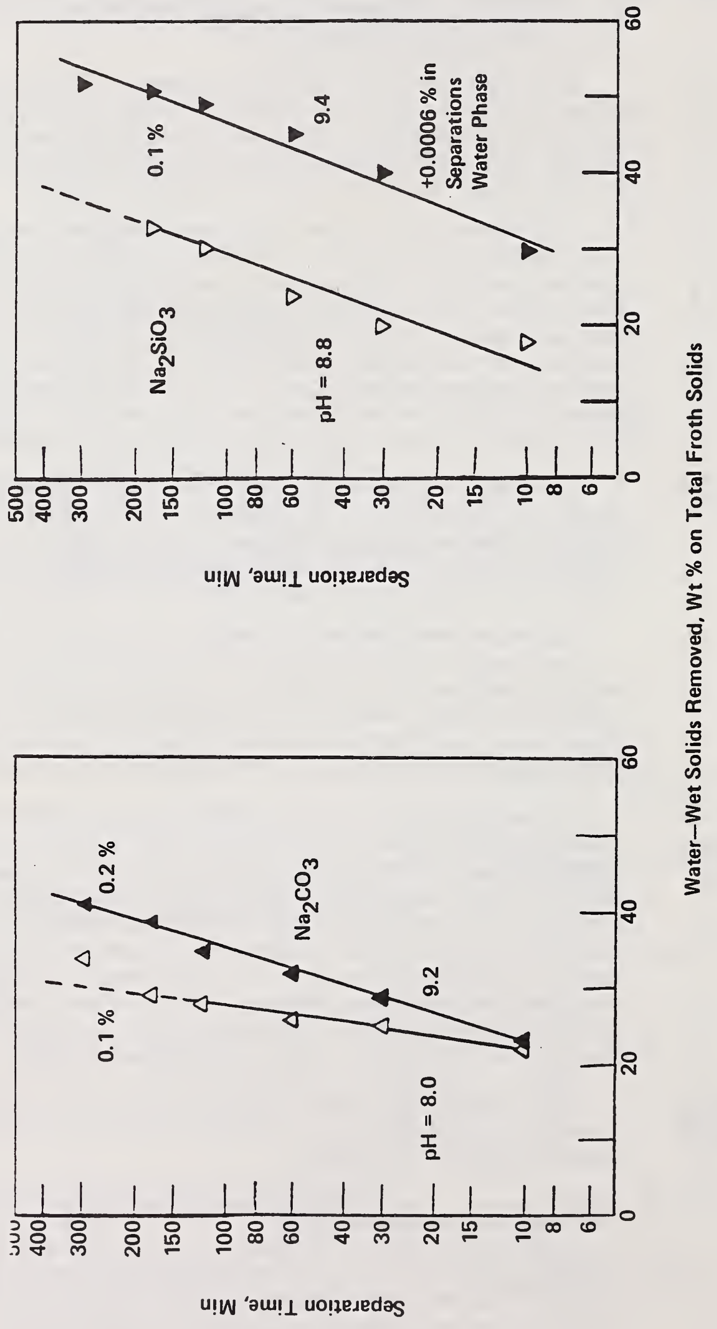
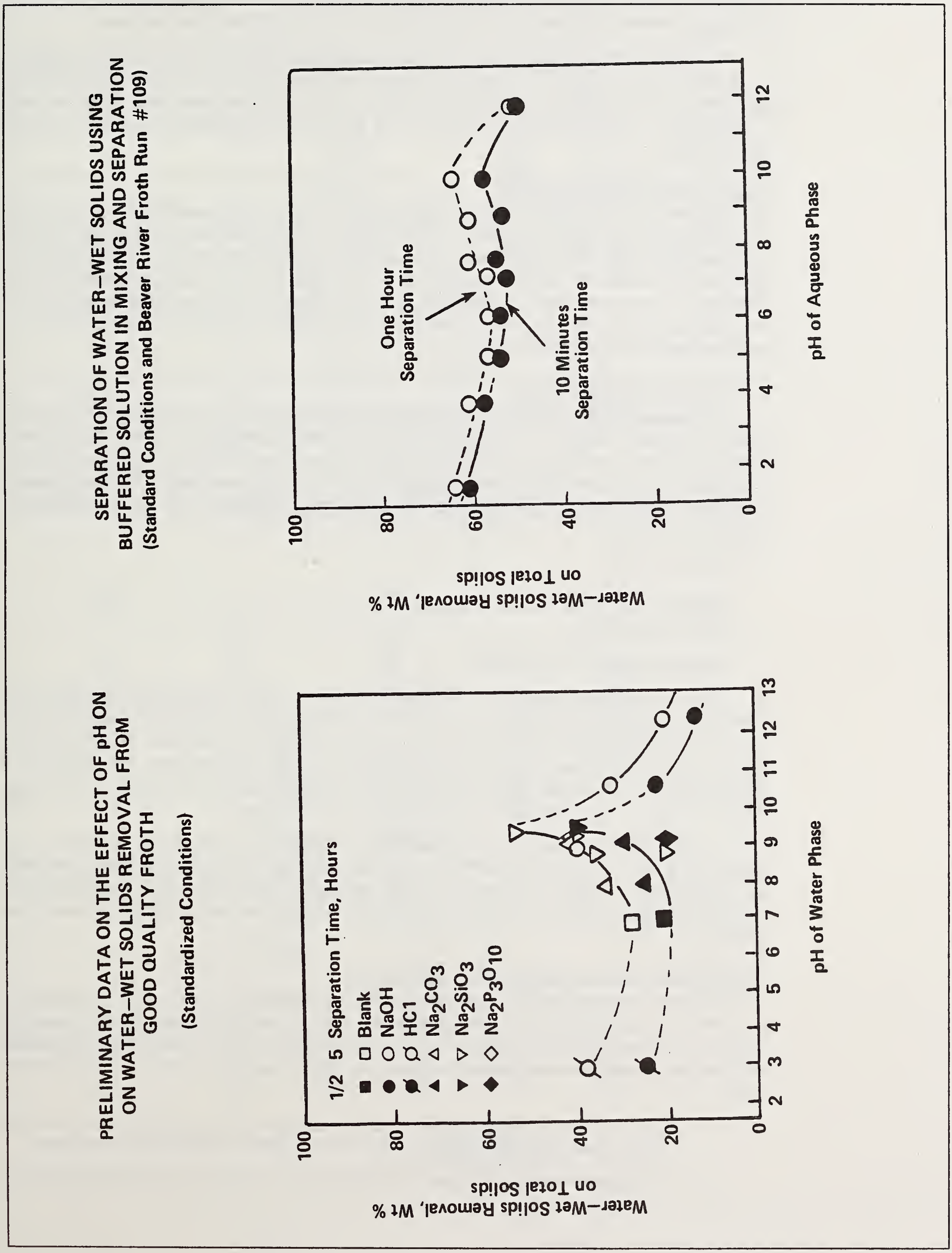


Figure 9-16

Preliminary Data on the Effect of pH on Water-Wet Solids Removal from Good Quality Froth



meshing screws, pug mills or tumblers, may be more ideal in effecting intimate contacting and shear at optimum low intensities of mixing than vertical mixers used in these small scale studies.

Studies in which the mixing intensity was varied indicated a maximum to occur at speeds high than the mild standard conditions adopted. Figure 9-18. The optimum solids removal is achieved a lower mixing intensity (~250 rpm) with sodium tripolyphosphate addition.

The greatly improved solids removal with good quality froth (~60%) and froth from Beaver River tar sand Run #109 (~75%) at higher mixing intensities, show this latter variable to be critical. Combined with the chemical energy of additives under optimum conditions about one third to three quarters of the total froth solids can be removed in considerably less than one-half hour's settling.

9-6-4 Solids In Separated Oil

The results are difficult to compare graphically as different total separation times were used in the different experiments. However, tabulating and averaging all results regardless of treatment, recorded in the table: Thus, it is not unreasonable to extrapolate the solids remaining in the oil-solvent phase after 10 minutes settling to be ~2 wt% based on oil. It should be noted that the solids content were obtained by ash analyses and pro-rated up to wet weight by dividing by 0.92. The solids derived by this ash technique will also reflect solids inherent in the oil, e.g. Fe, Ni, V etc. Thus this is the *total* solid content.

9-6-5 Water In Separated Oil

The results on water varied widely due to three sources of error: (a) sampling of 95% of oil phase by syringe resulted in occasional removal of small quantities of water, (b) frequent troubles with the Karl-Fisher test, and (c) difficulty in sampling the separated oil phase for this test. Earlier experiments suffered much from these errors. Later experiments, however, showed lower water values because of more controlled analytical procedures. However, tabulating and averaging results gave:

WATER IN OIL			
Separation Time, Hours	5	1	1/2
No. of Experiments	15	5	7
Average Solids, Wt% on Oil Only	5.9	5.9	4.8

Thus, it is not unreasonable to extropolate to water remaining in the oil-solvent phase after 10 minutes settling as 6 wt% based on oil or ~30% of total original froth water remaining in the oil phase. It will be appreciated that this value will increase at lower solvent to oil ratios of about 0.5-1.0. On the other hand, longer settling and larger settling oil phase zone, not attained in a small scale, may achieve an even lower value of 6 wt% water on oil, presumably by competing with natural carboxylic acids for the interface with emulsified water.

These points would have to be demonstrated on a larger scale, which could very well show better results than 2 wt% solids and 6% water on oil. However, even at these conservative levels, the water would be removed in the subsequent distillation process step to recover solvent for recycle, and the product oil would contain 2% solids, which is well below the process maximum of solids for coking.

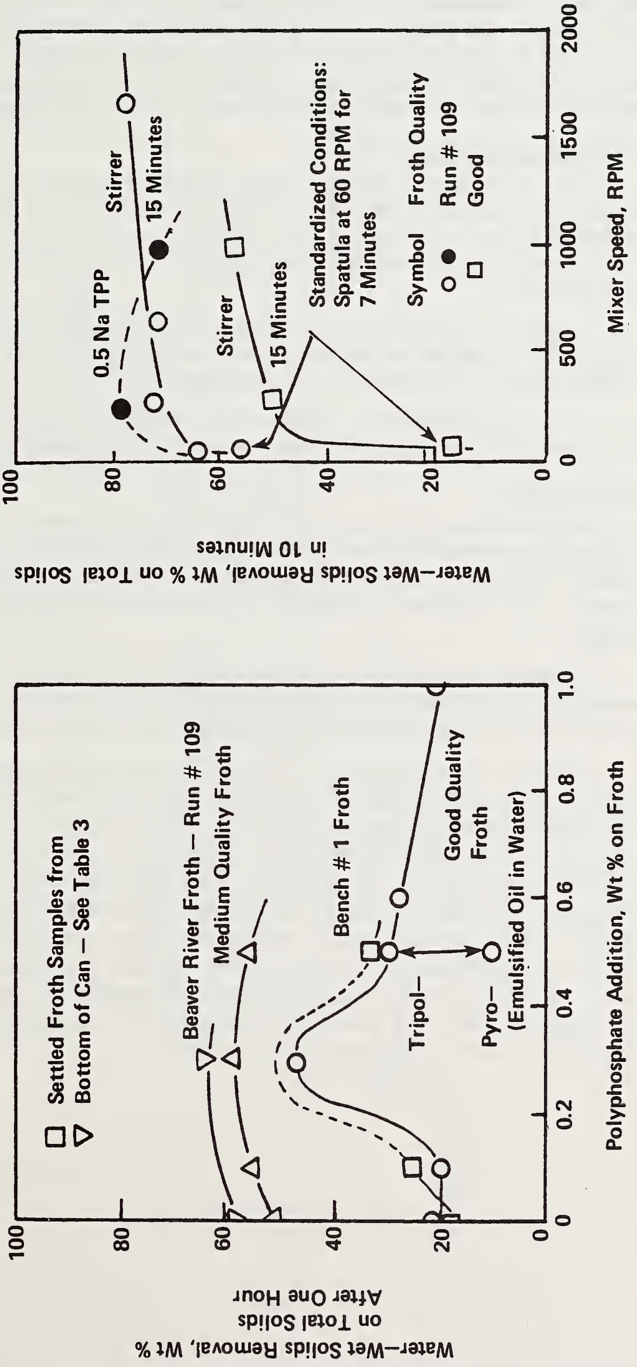
9-6-6 A Three Stream Operation (Figure 9-18)

The most important finding from these studies is that with all combinations of mechanical and chemical aids, the sludge-emulsion membranes which accumulate at the interface, cannot be entirely eliminated in dilution settling. Thus, it is necessary to initially demonstrated an operable and reproducible continuous three-stream process. The control objectives are summarized below:

- *1 An overhead oil phase product containing acceptable low levels of water and solid contaminants already defined by economics in studies of subsequent oil processes.*
- *2 A minimum sludge withdrawal from the oil-water interface to maintain operability.*

Figure 9-17

Effect of Sodium Phosphates Concentration and Froth Types, on Water-Wet Solids Removal



- *3 A maximum removal of water-wet solids in an underflow stream with water.*

A method of reducing the sludge-emulsion at the interface in settling is to remove it immediately after mixing prior to the separator. This might be achieved by a rotating screen or settling one at the end of the mixer. Thus, sludge could be withdrawn from the bottom of the mixer and prior to introduction into the settling zone. This approach was termed "an anhydrous solvent-dilution". The stream combined with any middling sludge removal from the separator would then be upgraded further in a secondary stage. This approach should merit some consideration in a study of mixer design. Also the technique of vibrating screen at the oil-water interface, should be given consideration in future large scale studies of separator design.

9-6-7 Projected Results

Based on average performance with a number of different Beaver River froths in these preliminary small-scale studies, projections have been made for expected pilot plant operations in Table 9-8. The possibility of doing better than these predictions exists, but will have to be demonstrated in larger scale operations particularly with reference to solids to oil ratios and mixing intensity.

The sludge or middle stream can be readily overcome by centrifuging. Centrifuging is the most positive separation method and results in essentially 99% oil recovery from this stream, at better quality than the separated oil-solvent phase.

It may also be necessary to recover some of the oil loss from the water-wet solids from settling. This could be done by, (a) centrifuging or (b) solvent washing as used in the laboratory.

9-7 Summary

Centrifuging is the best physical method for effective removal of water and solids contaminants from either hot water froth or agglomerates generated in primary separation of oil sands. Definition of oil recovery losses showed a minimum solvent/bitumen ratio of 0.7 is needed to effectively remove the bulk of the essentially clean bitumen in a single separation stage.

Further small but significant improvements in water and solids removal have also been observed in froth (agglomerate) cleanup by addition of small amounts of inorganic and/or organic additives in solvent dilution and settling with and without added water in the process.

Studies of solids transfer through oil-membrane-water interface using different Beaver River froths have demonstrated the possibility of developing an improved, optimum-energy, solvent-dilution gravity settling process. The approach is based on a three stream operation for the separation of the bulk of the solids within 10-30 minutes, as a lower phase in water. Further, 95% of oil and solvent is withdrawn as an upper phase containing <6% water and <2% solids based on oil. The water is about 30% of the original water in the froth and is removed in the subsequent distillation process step for recycle solvent recovery. The oil product containing ~2% solids could be processed directly, e.g. coking. The third or middle stream containing an emulsion of oil-solids-water can be readily separated by centrifuging,to produce a better quality than the settled oil phase with which it is combined prior to distillation for solvent recovery and dehydration. Larger scale demonstration is needed.

Figure 9-18

Flow Plan Combination Setlting - Centrifuging Process

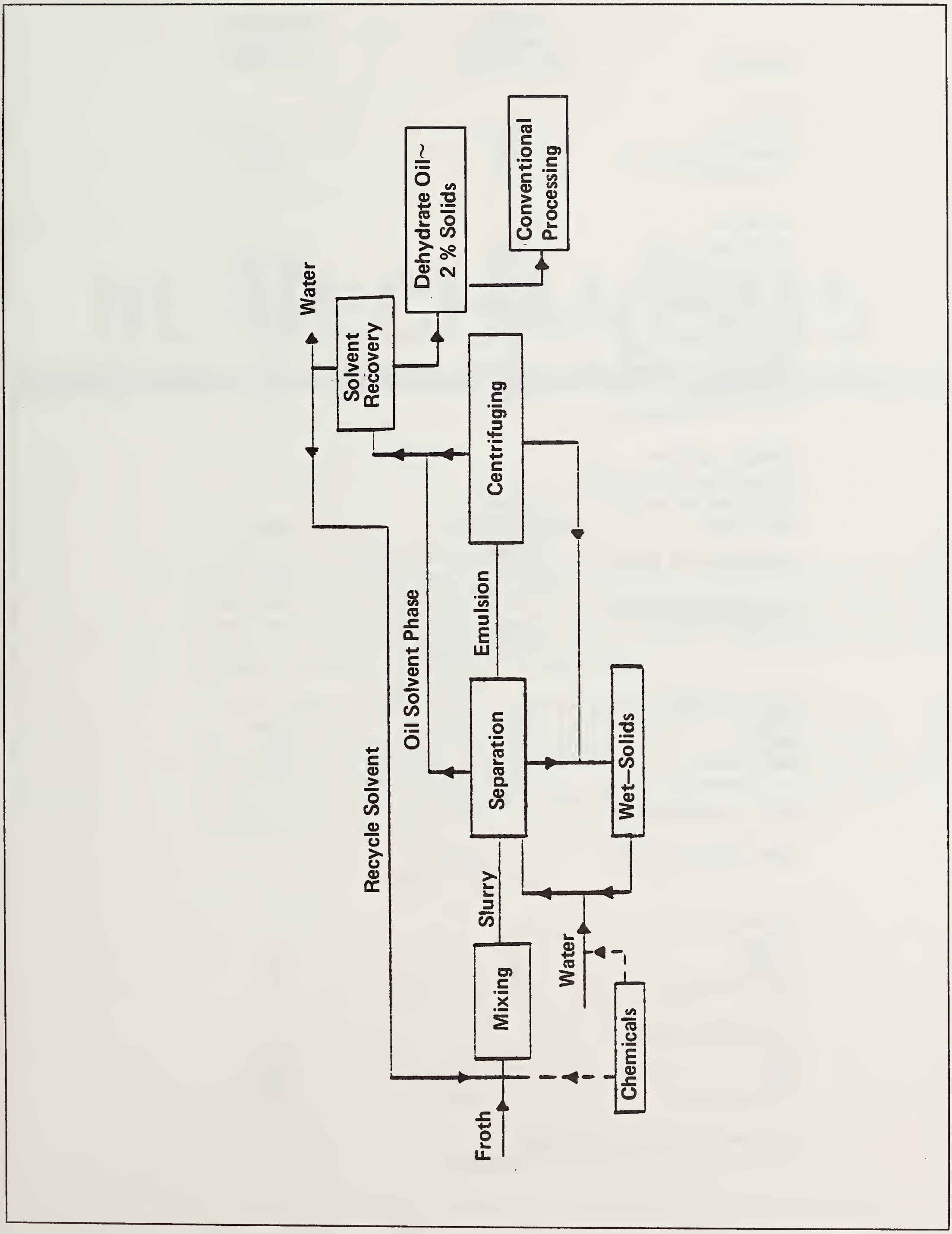


Table 9-8

Conditions and Results Projected for Upgrading Beaver River Froths in a Continuous Solvent-Dilution Process

Conditions	Used in Small Scale Batch Studies		Projected for Pilot Plant Operations
General			
Solvent Type	Xylene		Hy. Arom. Naphtha
Solvent-Froth Wt Ratio	1.0		0.5-1.0
Temperature °F	155		75-190
Mechanical			
Paddle Mixer Design	Vertical		Horizontal
Mixer Speed, RPM	300		100-1000?
Mixing Time, mins	15		≤5
Separation Time, mins	0-300(1)		10-30
Interfacial Vibrator	Yes		Yes
Screen Size, U.S. Mesh	16		≥16
Holes for Recirculation	None		Some
Vibrations, cps	60		~60
Minimum Amplitude, mm	1		>1
Chemical Addition			
Sodium Salts for pH Control			
Sodium Salts for Poorer Quality Froths	Hydroxide Tripolyphosphate Silicate		Same
Amount, Wt % on Froth	0-1.0		0.3
Average Results, Wt % on Total	**Without Chemicals**	**With Chemicals**	
Solids Removed in			
Oil Phase	15	12	Better
Sludge	25	13	- No
Water Phase	60	75	Ageing?
Solids Remaining in Oil	- - - 2% - - -		2%
Water Remaining in Oil	- - - <30 - - - (or 6 Wt % on oil)		-
Oil Recovery in			
Oil Phase	95	95	~95
Sludge(2)	4	3	~4
Water Phase (loss)	(1)	(2)	(1)
Sludge(2) Composition			
Water	- - - - 47 - - - -		Similar
Solids	- - - - 10 - - - -		- More
Oil Plus Solvent	- - - - 44 - - - -		Oil?

(1) Standard used to measure rate of solids removal.

(2) For secondary upgrading e.g. centrifuging, <10% original volume.

III. MECHANISMS

"Oil Sands" is not an homogeneous material. Precise generalizations on the natural state, properties, and separation behaviour is difficult. More often, in acquiring support data for an observed pattern, there are exceptions that disprove simple rules. It was therefore concluded that several interrelated factors govern oil sand separation behaviour. Further, a more exact understanding of the operative principles is needed to effect improvements in separation that may be developed and eventually realized on a commercial scale.

Hence, basic measurements of the interfacial energies of the oil sand components were carried out to determine their most probable phase relationships. The microstructure of the oil sands in the natural state was deduced from these findings. The effects of conditioning such as pH, temperature, ion concentrations, etc. on these interfacial energies were also measured, and compared with similar effects found in separation studies. The most probable mechanisms in oil sand separations were elucidated based on this integrated study. These findings are recorded in this Section as a reference for others who are pursuing this type of fascinating research.

10

INTERFACIAL

The two main approaches that have been used to determine the phase relationships are (1) the classical surface free energies at interfaces that show the most probable relationships of the different phases in the oil sands, as well as the relative importance of other conditions, such as pH, temperature, ions, etc., and (2) the magnitude and sign of the charge on the surfaces of particulate materials that controls the degree of dispersion-flocculation in a system, as well as the effect of ions on these states.

10-1 Surface Energies

The relation of phases and the energetic of boundaries present in the oil sands greatly affect the degree of processability for oil recovery. Basic interfacial measurements are therefore important to a better understanding of the oil sand structure and behaviour in separation. As the free surface energy in ergs per sq cm is numerically equal to the surface or interfacial tension in dynes per cm, then, the symbol θ is used to denote either of these surface properties.

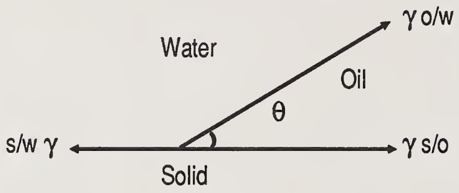
The surface energies can simply be illustrated by a small drop of oil resting on a solid surface immersed in water. This system is assumed to be in equilibrium, Table 10-1. The tensions are resolved horizontally. The amount of work or energy expended to separate oil from a solid ($W_{s/o}$) is defined, and a more useful combined relationship needing only the simplier measurements of interfacial tension and contact angle is derived.

Although, interfacial tensions of solids are difficult to obtain, they can give more direct evidence of the state of wettability of the specific solids in the oil sands. Hence some surface properties were measured to determine solids wettability. Also, the spreading coefficient of oil at a water-air interface that is involved in the attachment of air to oil enabling flotation, can also be calculated from these measured surface properties made at different conditions of pH and temperature.

Table 10-1

Surface Chemistry

Interfacial Tensions in an Oil-Solids-Water System Are:



Resolved:

$$\Upsilon s/w = \Upsilon s/o + \Upsilon o/w \cos\theta \tag{1}$$

Work of Adhesion:
(Dupre Eq'n)

$$Ws/o = \Upsilon s/w + \Upsilon o/w - \Upsilon s/o \tag{2}$$

Combined
(Young Eq'n)

$$Ws/o = \Upsilon o/w\,(1 + \cos\theta) \tag{3}$$

Adhesion Tension:

$$Aw/o = \Upsilon w - \Upsilon o/w \tag{4}$$

$$As/o = \Upsilon s - \Upsilon s/o \tag{5}$$

Condition for Water Wetting of Solids:

$$\Upsilon s/o - \Upsilon s/w - \Upsilon o/w > 0 \tag{6}$$

$$\theta > 90^{o} \tag{7}$$

$$As/w > As/o \tag{8}$$

Spreading Coefficient

$$So/w = \Upsilon w - \Upsilon o - \Upsilon o/w \tag{9}$$

10-1-1 Surface Tension

The intention of this investigation was to measure the surface tension, realizing that the platinum ring tensiometer method used was not of the highest accuracy. Further, as the oil is a diverse chemical mixture and variable, attempts at extreme accuracy with other methods was considered only for crosscheck. Subsequent pendant drop measurements confirmed the initial results reported here, as well as similar results with bitumen mixtures with practical solvents discussed in Section 2-4-4.

A series of surface tension measurements of various amounts of oil extracted from a sample of Mildred Lake oil sand in benzene and toluene solvents are shown in Figure 10-1. Extrapolation of the measurements at higher oil concentrations indicate a surface tension of 35.3 dynes per cm at 72°F for the extracted oil. The minimum found at the lower oil concentrations, i.e. 20-40%, might be explained in general by an increase in the degree of dispersion of some components, or complex results in an increase in surface activity.

Direct surface tension measurements on the oil at different temperatures were carried out, and also plotted in Figure 10-1. There was very good agreement between the surface tension measured at about 70°F and that found by extrapolation of data on solutions in aromatic solvents. At temperatures lower than about 67°F, the surface tension increased very rapidly indicating a transition point. At higher temperatures of 180°C used in the hot water flotation process the temperature was 21.5 dynes per cm.

The value of 35.3 dynes per cm at 70°F is higher than the average found for some 40 different crudes, i.e. 30.4 dynes per cm ± 11%. This, however, is not unexpected as in generally the surface tension is higher for more viscous crudes of higher specific gravity, and the oil from the oil sands possesses both these qualities. The surface tension measured falls in the range quoted in the International Critical Tables of 34 to 37.6 dynes per cm for Tar Oils (methods of measurement are unspecified).

The temperature coefficient from 100 to 200°F measured from the plot is approximately minus 0.085 dynes per cm per degree F, which is slightly greater than the slope of the lines for pure components, e.g. benzene = 0.070 dynes per cm per degree F.

10-1-2 Interfacial Tension

The purpose of this study was to obtain complementary data on interfacial tension, to that obtained on surface tension using the same sample of oil from Mildred Lake Oil Sands.

A series of interfacial tensions of various amounts of oil in aromatic solvents, i.e. benzene and toluene, gave a straight line relationship, Figure 10-2. The absence of a minimum in this linear correlation is explained by the hypothesis that a stronger bond of the polar components with the aromatic solvent occurred, which prevents adsorption of polar compounds at the interface.

The measured extrapolated value was 14.5 dynes per cm at 72°F, that when corrected for instrument bias, became 17.5 dynes per cm at 72°F. This value can be compared with results for 34 crude oils, at 70°F, which had interfacial tensions in the range of 13.6 to 34.3 dynes per cm, with an average of 20.4 dynes per cm and 7.3 dynes per cm as the standard deviation. The measured value lies in the lower part of this general range for these crudes. This is not unreasonable as in generally the interfacial tension is higher for more paraffinic crudes and oil from the oil sands contain appreciable quantities of aromatics, naphthenes and polar hydrocarbons.

Interfacial tension measurements at different temperatures, using a hot water jacketed cell, are also plotted in Figure 10-2. The scatter of the data about the solid line is due primarily to the difficulties in performing measurements. These difficulties arise from, (a) the densities of the oil and water being about the same, causing an undulating interface which is often very convex (downward) in shape and, (b) the tendency of the ring to slide at the interface and causing the measurement to be made with the ring at a very small angle to the verticle (not greater than about 5-10°). As the densities of the oil and water are about the same, the correction cannot be applied. However, this correction, as well as the instrument correction, is probably negligible

Figure10-1

Surface Tension of Mildred Lake Oil

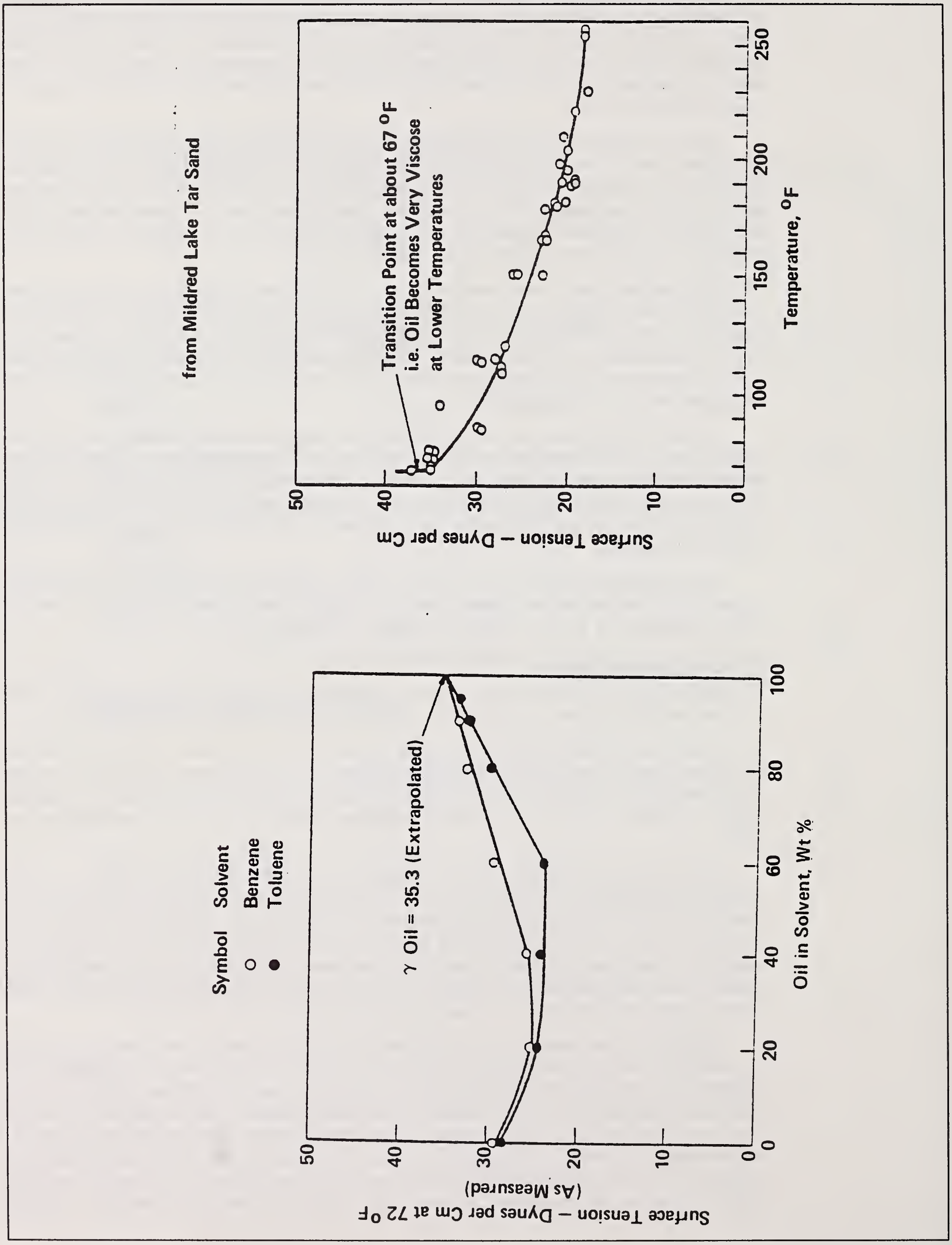
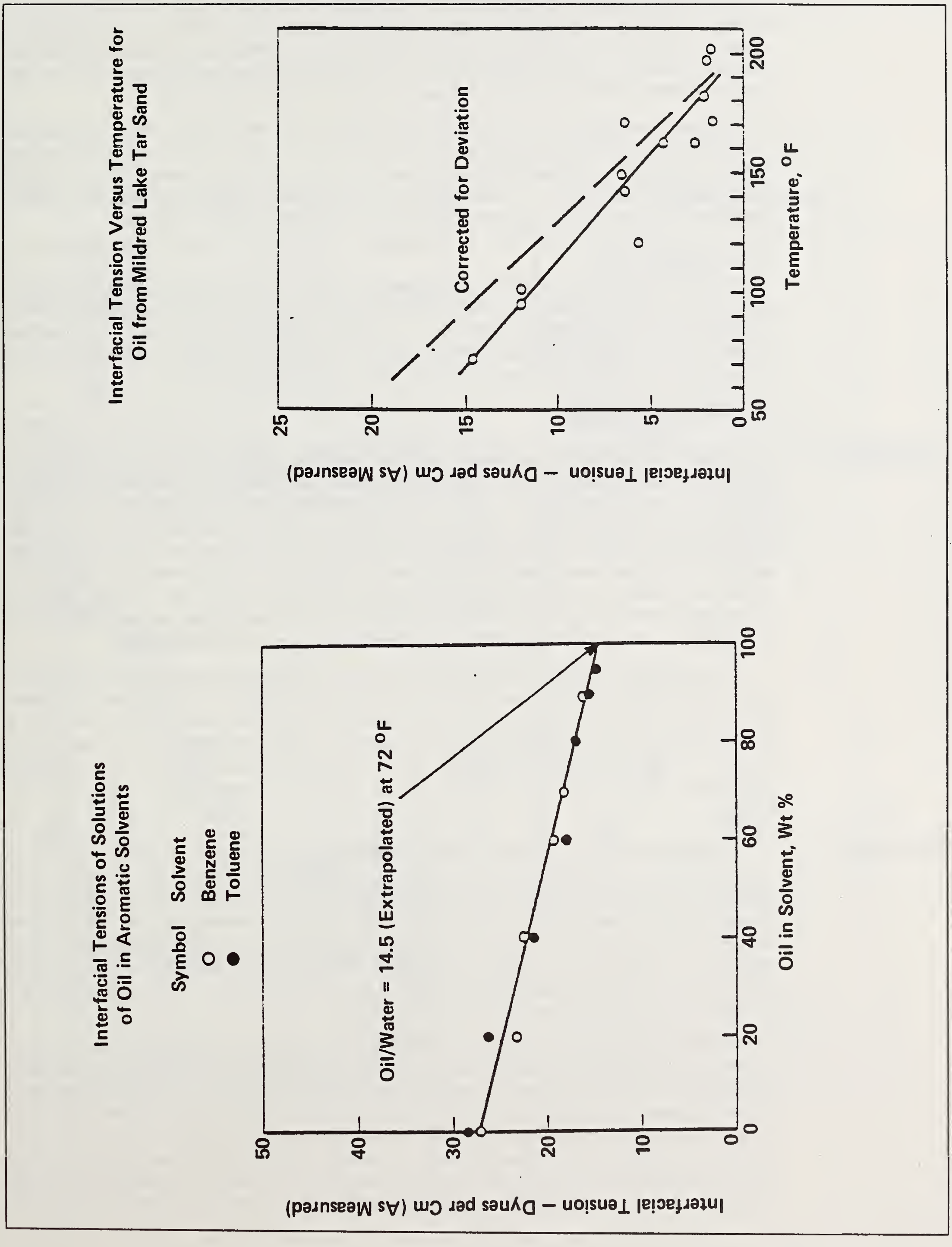


Figure10-2

Interfacial Tension of Oil



when the interfacial tension is small; i.e. less than about 10 dynes per cm, in view of the scatter of the data. Hence, the results at high temperature are approximately correct.

The temperature coefficients for the uncorrected data plot and the corrected line in Figure 10-2 are 0.11 dynes per cm and 0.13 dynes per cm, respectively, for the temperature range of 70-180°F. This compares reasonably well with the average temperature coefficients of interfacial tension with free vapourization for 34 crudes of approximately minus 0.2 dynes per cm per °F below 100°F and minus 0.1 dynes per cm per °F from 100 to 130°F.

Although the results of this study are only approximate, they do show that the interfacial tension at about 180°F, the temperature of the Hot Water Separation Process, is very low and hence a condition for emulsification of oil and water exists. This is substantiated by the high water content of the froth. Over 100 comparative measurements, using the pendant drop method, confirmed these preliminary measurements, but these data are no longer available.

10-1-3 Effect of pH

As pH in the slightly alkaline region is optimum for oil sand separation processes, interfacial tensions at 70°F, representing Sand Reduction separation, and 180°F, representing Hot Water Flotation were also measured, Figure 10-3. At 70°F, increasing pH by addition of sodium hydroxide decreased the interfacial energy. At 180°F, the interfacial tension measurements were too low at ~2.5 dynes per cm over the 7-11 pH range to make distinctions.

10-1-4 Contact Angles

(a) Advancing

Globules of oil formed underwater using a hypodermic syringe tend to rise at temperatures above 110°F and to sink at lower temperatures because the densities of water and oil are about the same at temperatures higher than 110°F. Care was taken to eliminate traces of air and gas from the oil and water, and also clay was removed from the oil by centrifuging. By controlling the temperature at above 110°F, a globule could be made to come to rest on a clean silica (glass) surface. The globule was initially a sphere and the angle in the water between the oil and the silica plate was zero. In time, the angle was observed to increase, and some "sticking" of the oil to the silica plate occurred at the point of contact. The final equilibrium contact angle after 3-4 hours was measured to be roughly 30° from pendant drop type, (See Photographs).

The increase in contact angle with time is due to the diffusion of naturally occuring surface active components in the oil to the oil-water and oil-silica interfaces. This absorption at the interface will be accompanied by a change in the interfacial tension. The same result was observed at room temperature, except that the process was slower, taking about 12 hours to attain equilibrium, i.e. decreased rate of diffusion due to the higher viscosity of the oil at the lower temperature. Further, substituting carbon for the silica plate gave a contact angle of 90° or greater.

(b) Receding

Centrifuged benzene extracted oil in clean dry glass jars was warmed to effect spreading of the oil over the whole bottom of the vessels. Solutions of known pH were then poured into the jars, and the systems was maintained at a constant temperature. In time, the oil rolled up into drops, which were approximately spherical in shape. Taking into consideration the oil contacting area with the glass and the shape of the sphere, it was possible to roughly estimate the contact angles. The receding contact angles as a function of the pH of the original solution in contact with the oil is shown in Figure 10-3. It should be noted that the curve will be compressed if plotted on the basis of the final equilibrium solution pH.

It was found that the contact angle is high in acid solutions and decreases to zero with increasing pH of the original solution. A large error range in the measurements of the contact angle is indicated which resulted from uncertainty in the actual measurement. Nevertheless, the curve of best estimates of the angle versus pH was quite well-defined and similar for both Area B and Hole 11 oils. It is interesting that the values for the receding contact angle in distilled water, i.e. pH equal to about 6.0, was about 20° which was similar to the advancing contact angle of about 30°, discussed before. The difference may be accounted for by hysteresis. It should be noted that in these studies the 1-2% benzene insoluble polar hydrocarbons were not included in the oil, that

Figure10-3

Effect of pH on Interficial Tension and Contact Angle

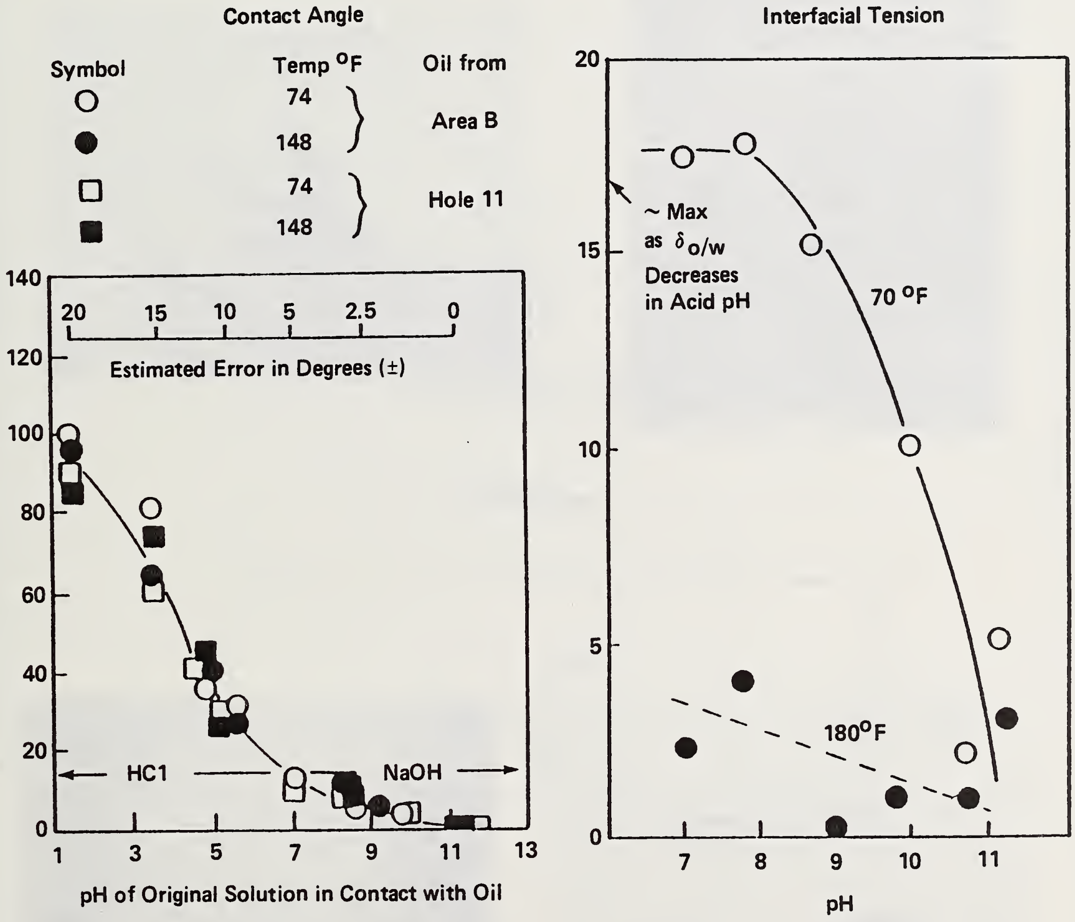


Figure 10-3 (b)

Oil Globule Behaviour (@9 pH)

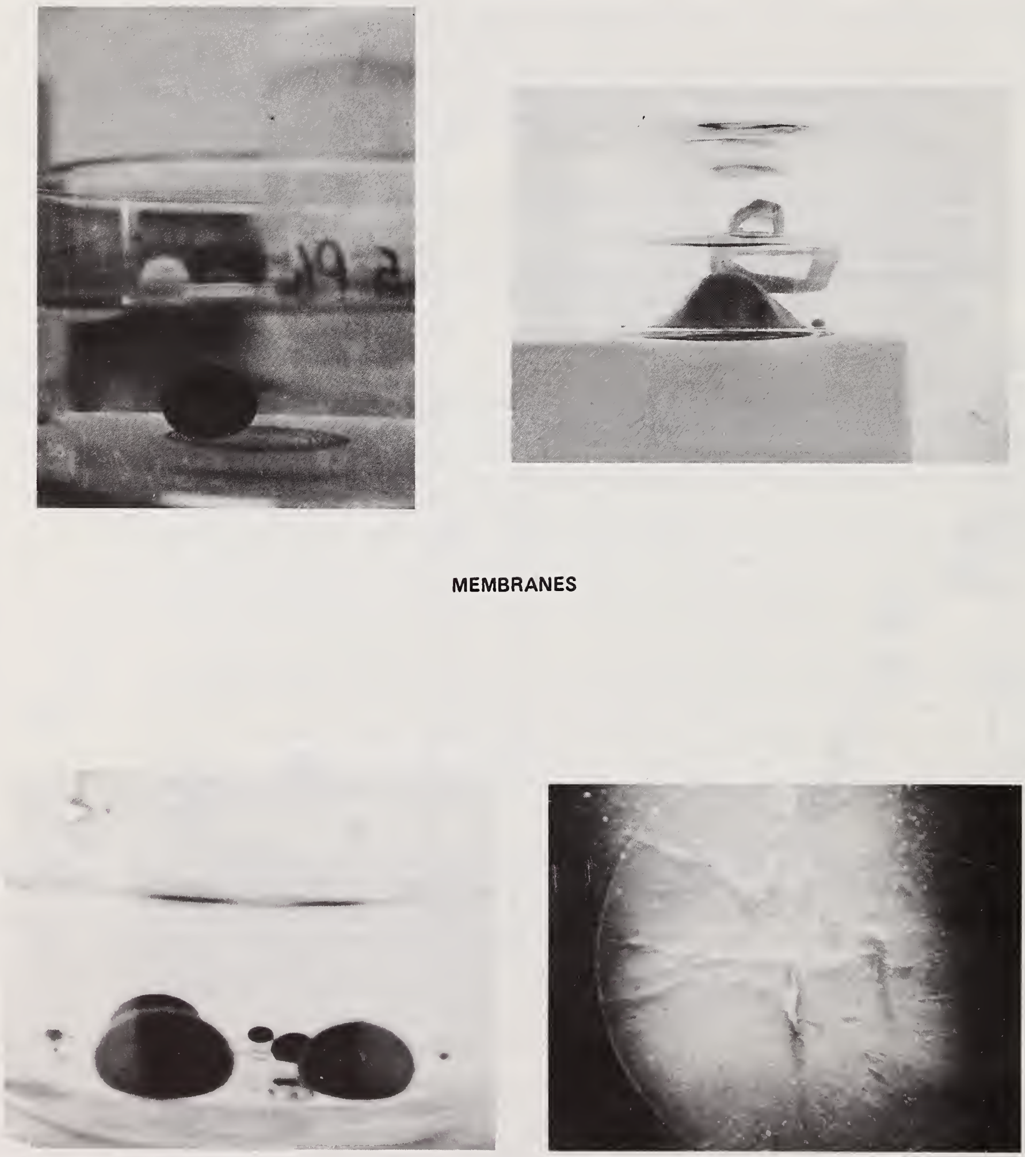


Figure10-4

Surface Tension of Water in Contact with Oil and Work of Adhesion of Oil

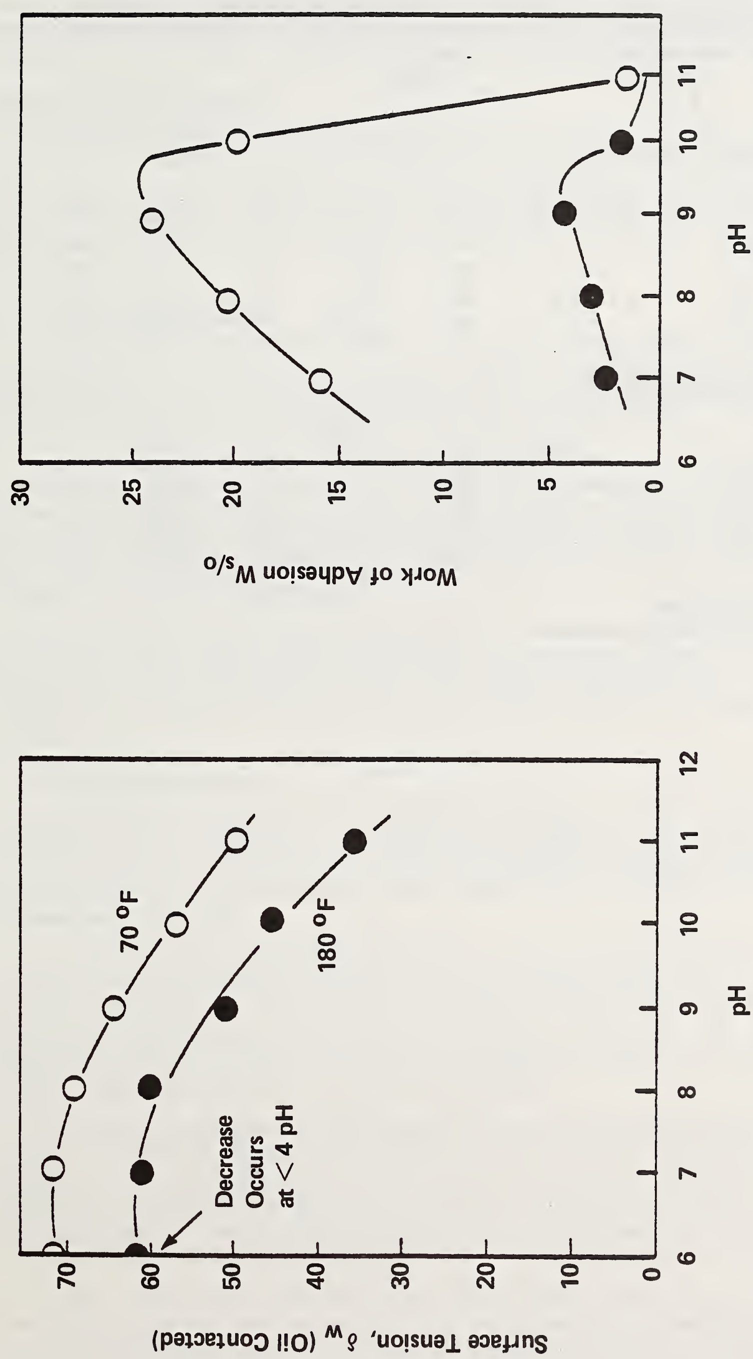


Table 10-2

Summary of Interfacial Properties

-------- Measured -------- ------------------------------------ Calculated ------------------------------------

Surface Properties Υo Υw
$\delta o/w$ ϕ θ $W_{s/o}$
$A_{w/o}$ $S_{o/a}$

					(180-Φ)	$\Upsilon o/w(1+\cos\theta)$	$(\Upsilon w-\Upsilon o/w)$	$((\Upsilon w-\Upsilon o-\Upsilon o/w)$
70°F (Sand Reduction)								
pH[1] 7	35.3	72	17.5	12	168	16	54.5	19
8	"	68	17.5	9	171	21	50.5	15
9	"	64	15	5	175	24	49	14
10	"	57	10	2	178	19	47	12
11	"	49	-2.5	0	180	1	46.5	11
180°F (Hot Water Flotation)								
ph[1] 7	21.5	62	-2.5[2]	12	168	2	59.5	38
8	"	59	"	9	171	3	56.5	35
9	"	52	"	5	175	4	49.5	28
10	"	45	"	2	178	1	42.5	21
11	"	36	"	0	180	0	33.5	12

(1) Adjusted with NaOH.
(2) Too low values (0-5) to make distinctions.

may have, if anything, decreased the surface activity measured. Temperature did not appear to have any applicable effect.

(c) Water Phase

The surface tension of the pH solutions that had been in contact with the Mildred Lake Oil was measured and plotted against the original pH in Figure 10-4. These values are more realistic as they reflect the interaction of soluble surfactants and sodium hydroxide used in separation, than those for a pure solution of sodium hydroxide that is essentially the same as water.

10-1-5 Work of Adhesion

The measured surface properties discussed above are summarized in Table 10-2. The calculated work of adhesion ($W_{s/o}$), plotted in Figure 10-4 as a function of pH, has a maximum at about 9 pH that is also the optimum condition for hot water flotation. The magnitude of the energy is substantially less at the higher temperature of 180°F indicating that any oil attachment to silica can be more readily stripped at higher temperatures - an advantage for the Hot Water Flotation process.

10-1-6 Adhesion Tension

A linear relation was found by Bartlett between the adhesion tension of different pure liquids against finely ground silica, as well as carbon black, and the immersion energy (or adhesion tension) of water in these liquids, Figure 10-5. The relationship for hydrophilic silica was directly proportional, whereas that for hydrophobic carbon was the inverse.

As most hydrophobic solids have the same interfacial tension with water, a generalization from this study, is that the trend in interfacial energy between pure liquids and hydrophilic solids are, as a first approximation, similar to that between pure liquids and water, that approved $\gamma_{s/w} = 0$. Experimentally, the average spread was determined to be +13 dynes per cm at 70°F for organic liquids, but Barlett concluded that because of possible errors in the indirect method used, the spread was more like 7 dynes per cm.

Immersion energies (Adhesion tensions) of water in oil $A_{w/o}$ as a function of pH were calculated from the data in Table 10-2, and used to derive corresponding values of adhesion tension against fine silica $A_{s/o}$, Figure 10-5. As these values, both at 70 and 180°F, are less than $A_{s/w}$ for water of 81.5 dynes per cm, then water wetting of solids appears to predominate over the 7-11 pH range.

10-1-7 Settling Volumes

The less a solid is wetted by a liquid, the higher will be the volume to which it will settle. Hence, the degree of wetting of oil sand solids can be measured by the volume to which they will freely settle in oil. As oil is too viscosity, extrapolation of settling volumes at various degrees (>50%) of solvent dilution can be used, similar to the technique used in surface tension measurement, Figure 10-1.

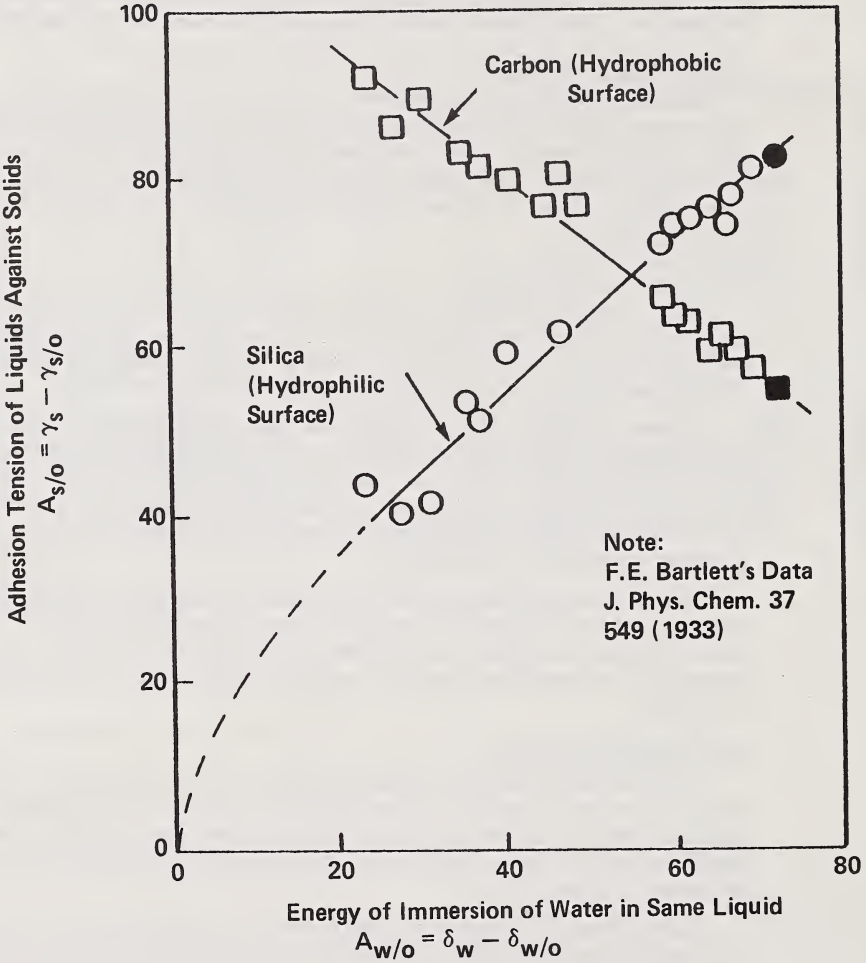
As solid wettability properties discussed above were for glass plate and finely ground silica, less than 325 mesh settled fines (~30 wt%) from a low grade oil sand (21A) of 6% oil content were used. These solids recovered from the oil sands were extracted with toluene and pyridine and were thoroughly washed with other polar solvents, e.g. chloroform, and dried. The well mixed clean solids were settled for equivalent times define by Stokes Law, in a number of pure organic liquids and in Mildred Lake Oil diluted with toluene.

The settling volume relationship for these fine solids with the interfacial tension of pure solvents is a straight line, Figure 10-6. The settling volume increased with increasing interfacial tension of the liquid. Settling volumes of these fine solids in oil diluted with 40, 50 and 60% toluene were identical. Hence, it was assumed that extrapolation to 100% was reasonable. The measurement of a settled volumes of fines in the black oil/toluene solutions was possible because a clear demarcation line at the top of the settled fines is just visible.

Hence, it was assumed, that the relative settling volume of fines in oil can be used with reasonable accuracy to determine the interfacial tension between fines and oil in the oil sands. The measured settling volume of 325 fines in oil was used to interpolate an interfacial tension of 26 dynes per cm at 70°F. This measurement is 8 dynes per cm greater than the oil-water interfa-

Figure10-5

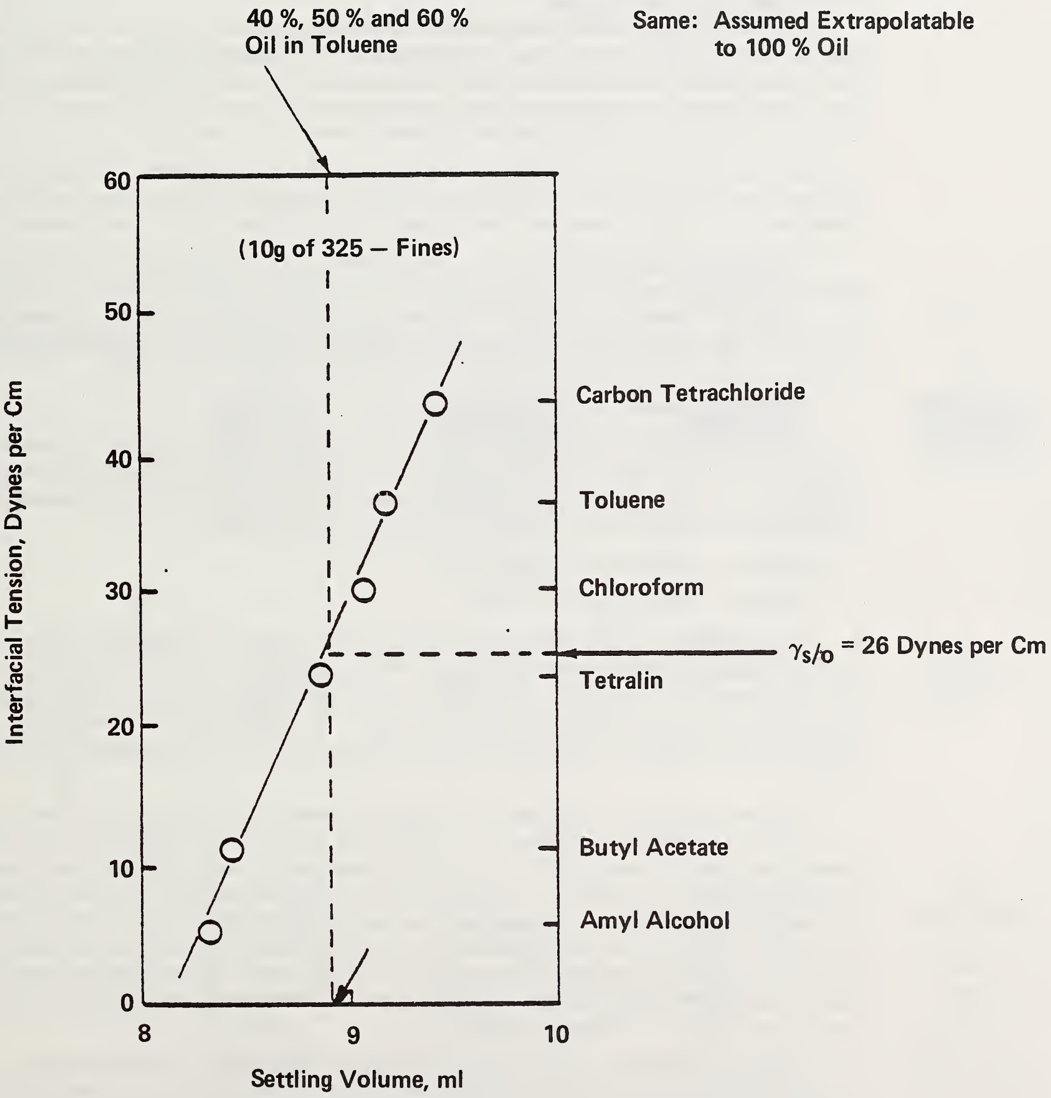
Adhesion Tension of Solids/Oil Interfaces



pH	$A_{w/o}$		"Interpolated"	$A_{si/o}$
	70 °F	180 °F	70 °F	180 °F
7	55	60	67	72
8	51	57	65	70
9	49	50	63	64
10	47	43	61	58
11	46	34	60	50

Figure10-6

Adhesion Tension of 325 - Fines Against Oil Settling Volumes



cial tension of 17.5 dynes per cm, that approximately agrees with Barlett's conclusion on the energy spread. Further, this surface energy for fines, that is mostly clay minerals, against Athabasca oil is only slightly lower than those of silica against other crude oils reported in the literature of about 29 dynes per cm.

This tends to support the generalization that hydrophilic solids have similar surface energies, and those of sand and fines, that are mainly clay minerals are similar. Long term settling at 180°F gave only a marginally lower value of 23 dynes per cm indicating little effect of temperature.

10-1-8 Conditions for Wetting

The main condition for oil sands solids to be water wet (equation 6: Table 10-1) must be positive. Substituting the experimental values obtained, the spreading coefficient for 70°F indicates that the solids in the oil sands will go freely from the oil into the water at formation conditions, since energy is not needed. Additional measurements on contact angles (equation 7), and calculations of literature adhesion tensions (equation 8) support this conclusion.

Hence, the generalized statement that the bulk, if not all, of the solid surfaces in the oil sand microstructure are water-wet is considered valid. Further, essentially complete water wetting occurred back at the time of formation. However, the oil is too viscous to flow and accumulated.

The fact that extraction processes work is consistent with this concept that the oil in the oil sand is already separated from the solids by a thin film of water. A "Separation Process" is therefore a physical method or technique of separating the solids components with water, and recovering bulk oil with some contamination by solids and water. Hence, it is most important that tar sands are not allowed to "dry out" after removal from the natural formation.

This can be illustrated by the following experiment.

Using the four main components of the oil sands, in their relative amounts, an attempt to reconstruct the oil sands was made in the following manner. The four dry separated components, (solid dried in an oven at 220°F) were mixed together in two different orders of addition to give two synthetic tar sands. The order of addition in mixing were as follows:

Synthetic A: water - clay - sand - oil

Synthetic B: clay - sand - oil - water

These synthetic oil sands were then mixed with toluene solvent and poured into water to effect separation of the oil. The separation pattern for the Synthetic A oil sand, in which the solids were first wetted with water, was very similar to that with natural oil sands of high connate water. This is shown diagramatically in Figure 10-7. The larger amount of emulsion in the separation with Synthetic A oil sand, probably reflects the difficulty of "rehydrating" over dried clay.

The poor separation patterns obtained with the synthetic B oil sands, in which the solids were first wetted with oil, was found to be similar to the low water "dried" oil sands. This showed that when the water film capillaries on the solids of the natural oil sands are depleted from exposure, they then become "effectively oil wet", and are difficult to rewet with water. In the case where the solids are completely oil wet, and energy is not needed to rewet the solids with water, work has to be done to first overcome the cohesion energy of the oil surrounding a solid particle to effect contact with water, before rewetting occurs spontaneously with peeling back of the oil layer. Silica, that at one time has been water-wet, retain some residual hydroxyl ions on the surface that facilitates rewetting.

However, the example of "dried" oil sands is more complex in that an acid pH condition can develop, and clear solids separation will only occur if the oil sands is severely mixed with a hot solution of a suitable alkaline inorganic additive. Even then, separation is incomplete and the oil phase is more like an agglomerate than a froth, and hangs just under the surface rather than floats. It is high in solids of about the same distribution as the original oil sands and the ashen solids from the froth usually contain appreciably more iron than the separated solids. This will be discussed further in connection with the mechanism of aging by dehydration and oxidation.

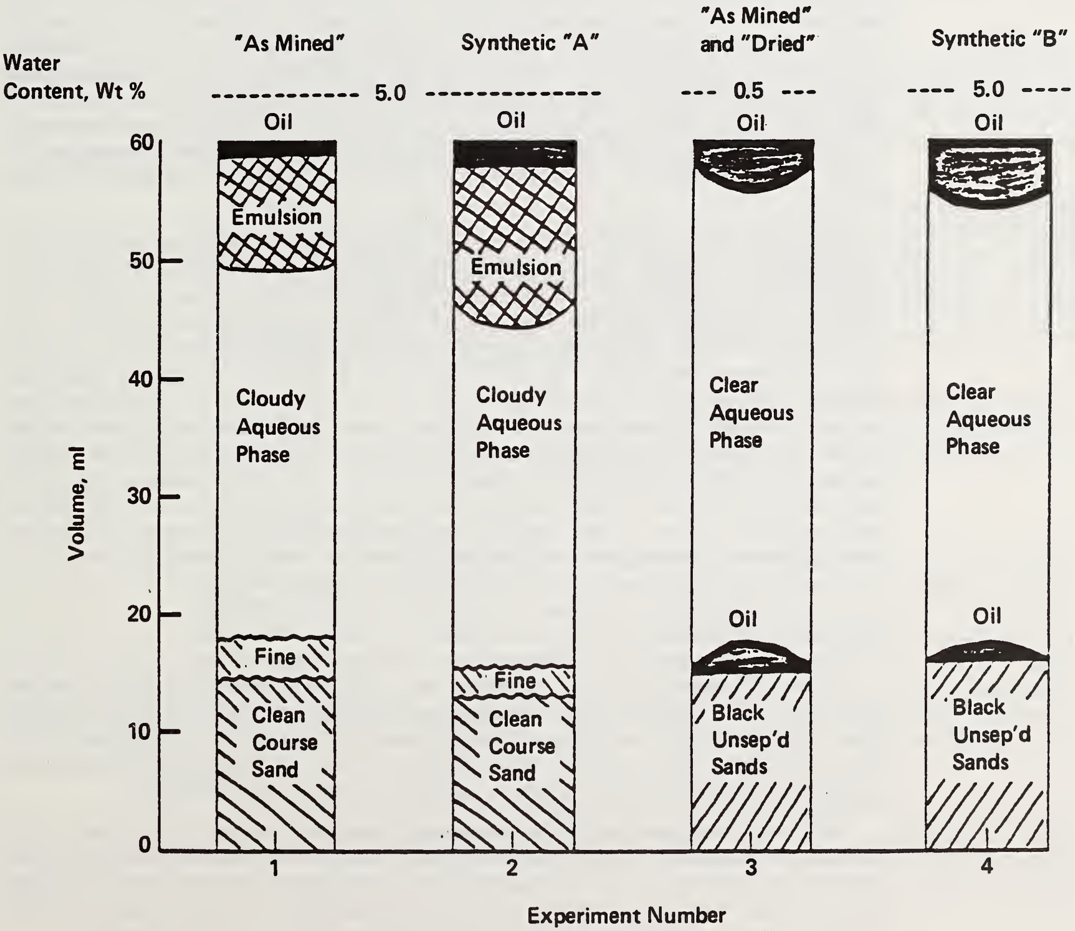
Figure10-7

Solids in Tar Sands Are Already Water Wet

Note: Tar sands were mixed with 30 Wt % solvent (i.e., 2:1 solvent to bitumen ratio) — one minute mixings. Added to excess water shaken for 10 seconds — settles for 5 minutes, at 140 °F

Order of mixing components of synthetic tar sands:

Synthetic A — Water + Clay + Sand + Oil
Synthetic B — Clay + Sand + Oil + Water



10-1-9 Spreading Coefficients

The gravity of the oil in the oil sands is shown in Section 2 to be very close to that of water at the temperature of 185°F used in the Hot Water Flotation Process. Hence any attachment of solids will increase the tendency to sink, but attachment of air will effect flotation. The amount of gases in the mined oil sands in contact with the oil particles, is not known. However, separation studies on the need for the right type of mixing to occlude sufficient air for flotation have indicated that aeration is needed for efficient oil recovery.

Oil will spread at an air/water interface if the speading coefficient (S) is positive (Equation 9: Table 10-1). Values of S are calculated from measured surface properties in Table 10-2. The tendency to spread decreases with increasing pH, and with lower temperatures even ignoring the large effect of viscosity. Hence, the spreading tendency of oil to occlude air is greater at the conditions of the hot water process. Ideally, S is maximized if the interfacial tension of oil-water is zero i.e. a condition for emulsification of oil-water. Further, studies of aeration in devising laboratory similarities of the Hot Water Process have shown that smaller bubbles are more effective and dissolve gas in the aqueous solution that can nucleate on oil particle surfaces are best.

This spreading effect at room temperature can be readily seen by placing a drop of water in contact with a small amount of tar sands on a microscope slide and observing the oil film which rapidly spreads over the drop of water. Another example of this spreading effect has been observed at even lower temperatures, i.e. 50°F.An "agglomerate" containing 62 wt% solids and 38 wt% oil was washed with cold water from the mains in a beaker. Some of the air in the stream of water flowing through the beaker impinged on the surface of the agglomerate and an oil film spread around the bubble occluding it to the surface. When sufficient air had become attached to the surface, the agglomerate floated. This low temperature flotation is most interesting and occurred in about one hour. This separation time was reduced to a matter of minutes with dissolved CO_2.

Small globules of oil, that are formed at the surface of aqueous solutions, initially spread. The equilibrium condition being the globule with a very thin surface film of oil over the surrounding larger aqueous phase. The lowering of the surface tension or surface pressure, i.e. π, of these very thin films have been measured. In contact with distilled water at 70°F, π was 17 dynes/cm, and with 1% solutions of sodium tripolyphosphate and sodium silicate, π was 41 and 45 dynes/cm, respectively. At 180°F, π was 19 dynes/cm with distilled water, and 8 dynes/cm with both sodium silicate and sodium tripolyphosphate. These measurements were made immediately after the formation of the films, however, the thickness and pH are contributing factors, which were not kept constant. The purpose of recording these data is to show that the presence of sodium salts in the aqueous phase give marked changes in the surface pressure. This suggests that these films have orientated ionized polar groups at the interface at low temperatures and higher rigidity. On the other hand, at higher temperature the presence of silicate and tripolyphosphate increases the tendency for film rupture that could be a possible explanation for better quality froth with these additives in the Hot Water Flotation Process.

10-1-10 Summary

The evidence presented above support the viewpoint that the bulk, if not all, of the solids, in the oil sands are water wet, and optimum separation can be achieved at ~9 pH. This is consistent with our overall experience of oil sand-water separation processes. This conclusion, however, goes further in indicating that the cause of poor separation is due to other factors and not oil wetting of fine solids in the oil sands. Also in connection with the Hot Water Flotation Process, the spreading coefficient is positive enabling the occlusion of air in oil to aid flotation.

However, the role of ions, for example, are not taken into account in this surface energy treatment, and are even excluded in the preparation of the oil sand components used to make surface property measurements. Hence, as other data is needed to account for these effects, then surface charge measurements on small particles of oil, and solids were carried out in an attempt to obtain a better understanding of these interfacial relationships in oil sands separation.

10-2 Zeta Potential

As the concept of zeta potential is important for a better understanding of oil sand-water separation processes, a brief theoretical background is given to outline its significance, before presenting the data obtained. *(Appendix V6)*

10-2-1 Concept

Simply, zeta potential is the practical measurement of the potential difference between the surface of a suspended oil or solid particle, in the case of oil sands, and the continuous aqueous phase. As most particles in water are negatively charged due to the high dielectric constant of water, this is illustrated in the Appendix VF for an electronegative particle.

The "Stern" or "double layer", about which comparatively little is known, is due to an excess of negatively charged sites on the physical surface and/or adsorbed negative ions (OH^-), that is surrounded by a layer of positive ions (H^+, Na^+) attracted either from the immediate surface of the particle or from the bulk of the aqueous phase. This attraction is greatest near the surface of the particle creating a rigid "double layer" that repel positive counterious in the diffuse layer as well as ions in the bulk phase. Negative ions both inorganic and organic are both attracted into and maintained in the diffuse layer by attraction/repulsion of the double layer.

The nature and size of these negative counterions can influence the thickness of the diffuse layer. However, the effect of polyvalent cations is by comparison tremendous in their power to reduce zeta potential that is a function of the inverse power[1] of their valency.

The measured zeta potential is actually the potential at the separation of the "shear" plane of the double layer and the diffuse layer. Thus, it is also a measure of the diffuse layer per unit surface of the particle and of its thickness. As such, it is a measure of force and distance in the repulsion-attraction of individual particles corresponding to dispersion-flocculation, when the zeta potential is either greater or smaller than a limiting value, e.g. ~15 mv.

Hence, for a discrete hydrophilic clay particle in an aqueous phase, there is a relationship between the practical thickness of the double layer, the type and concentration of the salts in the aqueous phase, and the zeta potential, see Appendix VF. These are only approximate scales as the thickness of the diffuse layer that cannot be determined exactly. In general, the zeta potential decreases and the "double" and "diffuse" layers collapse with increasing concentrations of salts in the aqueous phase. This trend is from dispersion to flocculation, and also represents a decrease in the "hydration" layer on the surface of a particle.

In general, zeta potential measurements on oil and solid particles are essentially "static" or "equilibrium" surface state properties, as a function of ionic species and concentrations in the aqueous phase. Hence, zeta potential data has significance both in the microstructure of the oil sands in the natural formation, as well as in separation of phases in processing.

10-2-2 Oil Particles

Discrete oil particles, like solids, have negative surface charges, Figure 10-8, except at high and low pH where the double layer has been destroyed by high ion concentrations causing oil agglomeration. Both curves show a maximum at ~9 pH for these two oils from different oil sands. The similarity in shape of the curves indicate that the same types of naturally occurring anionic surfactants occur in both samples. The higher zeta potential of Hole 11 oil indicates more polarity of the natural surfactants in this oil. It should be noted that normally after soxhlet extractions of oil sands with toluene, more surfactants remain in the solids from low grade oil sands like Hole 11 than high grade oil sands like Area B that are removed by more polar solvents e.g. pyridine.

These observations tend to support a generalization on their higher polarity as well as that more surfactants of higher activity occur in lower grades. As the oils are very similar in other compositional aspects, it appears that the higher polarity could have resulted from more oxidation at the time of the natural formation of oil sands. Although there is the other less probable possibility of oxidation due to dissolved oxygen in surface waters penetration the formation or to exposure during mining of this area. As oil oxidation rates are generally very slow at ambient conditions, only minor oxidation effects would be expected in a commercial mining operation.

---

[1] *e.g.:Schulze-Hardy rule = 6, Debye-Huckel = 2*

10-2-3 Oil/Salt Effects

The same general effect of drastic reductions in zeta potential with higher concentrations of typical salts that can occur in the natural state or in separation is shown in the lower plot of Figure 10-8 for suspended oil particles. Trivalent metal ions, such as ferric iron, an oxidation product of naturally occurring ferrous iron from a relatively soluble mineral source such as siderite ($FeCO_3$), can cause charge reversal.

It is proposed that effective oil association with solids can occur through this type of bonding of positively charged sites on the solids with surfactants in the oil, i.e. "wetting" by "tagging" mechanism.

SOLID-POLYVALENT METAL ION-SURFACTANT-OIL

Divalent calcium is substantially more effective than monovalent sodium in reducing zeta potential in accord with the theoretical relationship that the concentration of a salt is proportional to an inverse power of the ion valency. The power is 6 in the Schulze-Hardy rule and 2 in the Debye-Huckel treatment. In any case, the power of a polyvalent ion to reduce zeta-potential is therefore tremendous, and consistent with those results. Hence, divalent ions (Ca^{++}, Mg^{++}) that occur in the water phase, and in ion-exchanged clays, as well as colloidal alkaline precipitates of these ions, can all contribute to poorer processability by association with oil. This is even more true for polyvalent ions (Fe^{+++}, Al^{+++}). Further, all these ions can participate in the solids "wetting" bridge, discussed above, leading to weighting the oil particles with solids that inhibit flotation in the Hot Water Separation Process.

10-2-4 Pure Minerals

The zeta potential of pure[1] tourmaline, rutile, ilmenite, zircon suspensions as a function of pH has been measured and the results are recorded in Figure 10-9. There is a remarkable similarity in the shape of each curve although there are small differences, considering the wide variations in chemical composition. Similar data were also obtained for siderite, staurolite and kyanite (data not shown).

At high alkaline pH the minerals are not charged. At about 10 pH, the zeta potential is at a negative maximum. This was consistent for all the minerals inspected. It is interesting that this also corresponds to about the optimum pH for hot water separation. Under acid conditions, the zeta potential showed a positive maximum. At very low pH's of about 1 the zeta potential was again zero. The pH of the positive maximum varied slightly for different minerals, as well as the more important isoelectrical point; i.e. the pH at which the sign of the charge changes from negative to positive.

In the literature, zeta potentials of pure minerals and results of flotation experiments have been interpreted in terms of the isoelectric point. The general pattern found in our studies indicates that most heavy mineral types will be concentrated in the froth. Any selective flotation effect e.g. zircon concentration will presumably occur from some other factor, such as adsorption of surfactants on the mineral surfaces.

Further, the data indicates that separation of heavy minerals by flotation will be very difficult due to very small differences between the isoelectric points without even considering the wide range of particle sizes and probable differences in surface states.

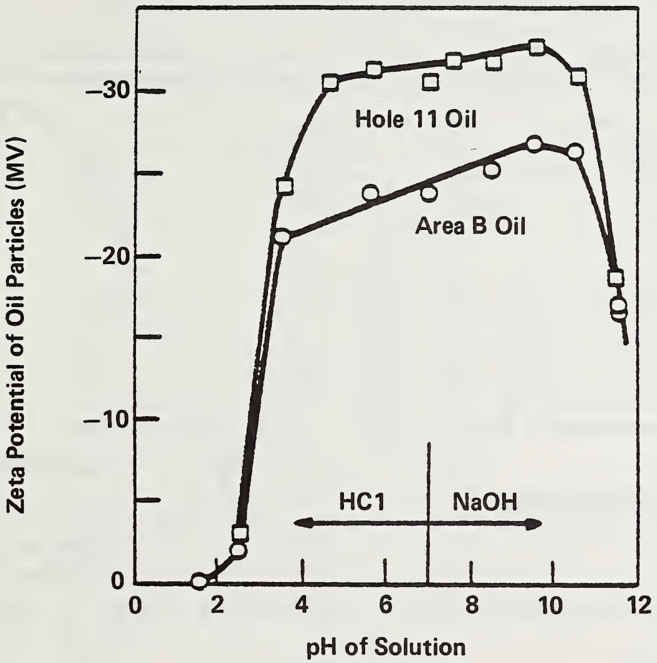
10-2-5 Mineral Suspensions

Zeta potential measurements were made on various fines (clay lens) samples and all oil sand samples, as well as water phases from some hot water flotation studies. In view of the abundance of particles, it was necessary to carry out these micro-electrophoresis experiments under dilutions of approximately 50 times of the supernatant liquid. The supernatant liquid consisted of

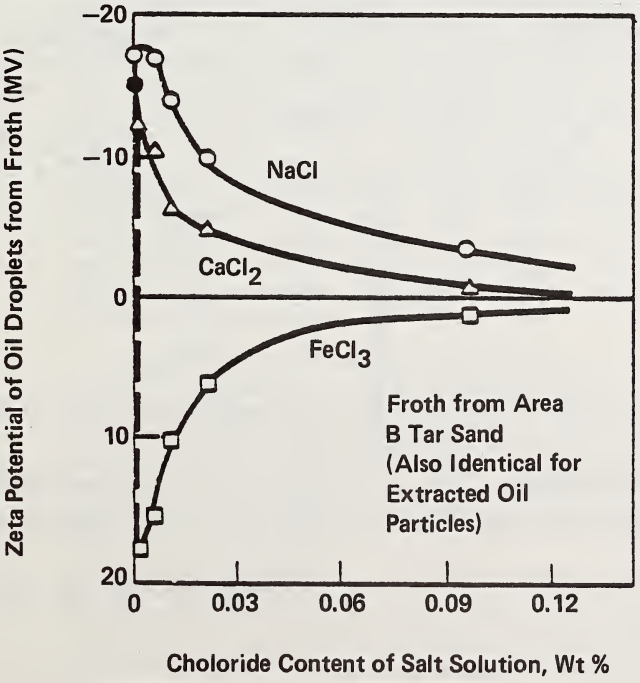
[1] *obtained from Australia and USA areas*

Figure10-8

Zeta Potential of Benzene Extracted Oil Versus pH



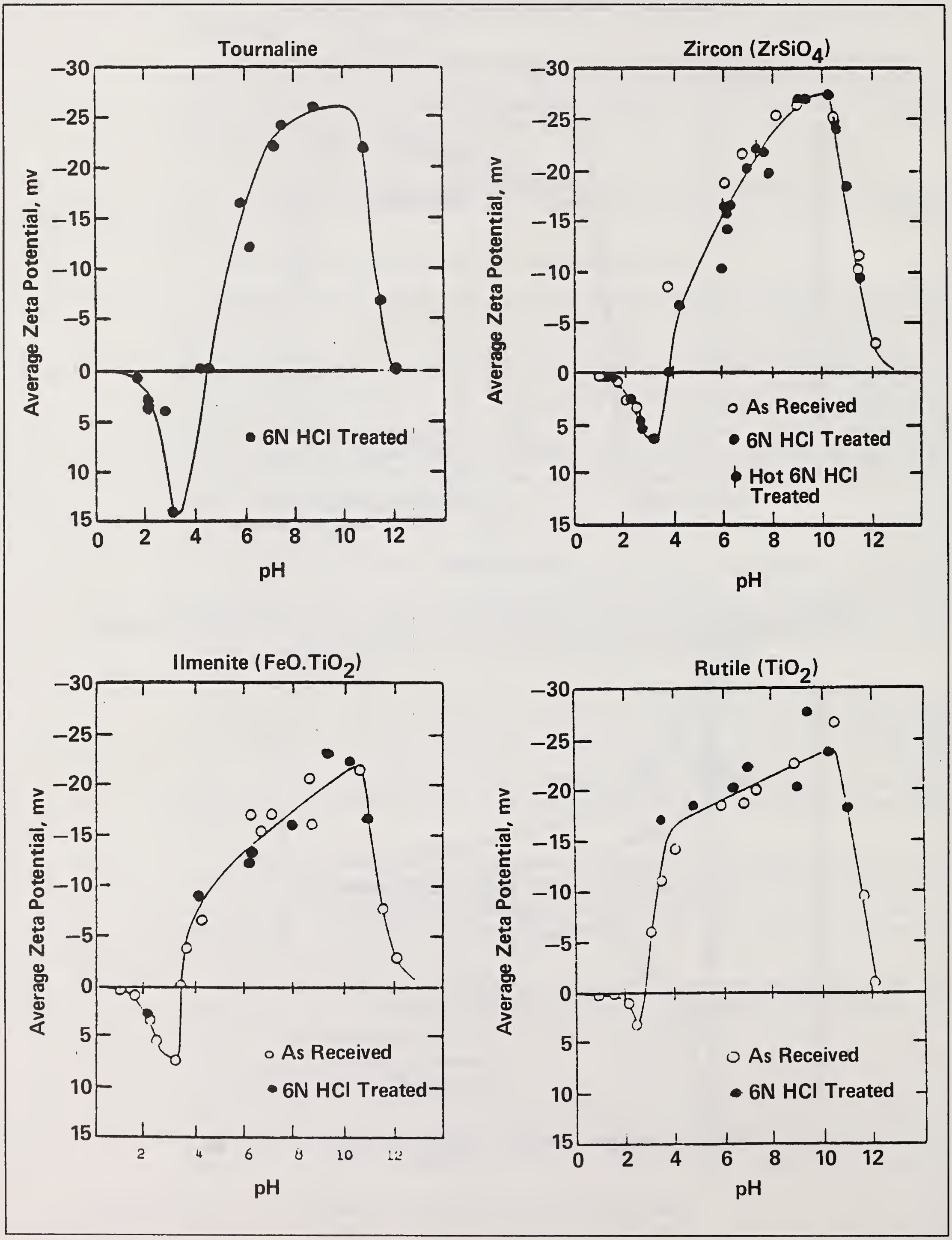
ZETA POTENTIAL OF OIL FROM FROTH VERSUS SALT CONCENTRATION



Froth from Area
B Tar Sand
(Also Identical for
Extracted Oil
Particles)

Figure10-9

Zeta Potential vs pH Relation for (<10 µ) Mineral Suspensions



50 g of tar sands in 200 ml of distilled water followed by a settling period of about 20 minutes. All pH measurements were made on diluted supernatant liquid.

The zeta potential of most minerals is negative. Only a few very highly charged positive particles were observed in hundreds of determinations. The degree of negative charge is a measure of the dispersion of the system. In general, a zeta potential value from -20 to -40 represents a moderately stable system and any zeta potential below about 15 is relatively unstable.

Solid particles, mostly clay minerals from the oil sands have zeta potentials in the range of -10 to -30 mv. An example is shown in Figure 10-10 for fines suspensions from a characterization study on oil sand. Although, there is considerable scatter in the data, a general increase in zeta potential (dispersion) with increasing pH appears to exist when compared with fine silica data from the literature that shows a characteristic type maximum curve.

These particular data that are typical for oil sands are only borderline in stability with an average of -19 mv. These zeta potential values seemed reasonable enough since most of the fines settled out overnight, and indicated that the clay in the prepared samples was partially flocculated. However, a small quantity of very fine material remained in suspension for extended periods of months, i.e. colloidal. Treatment of these suspensions with very small quantities of sodium salts, e.g. sodium silicate, resulted in greater dispersion of the clay minerals and high zeta potentials of -40 to -50 mv for the finely dispersed particles. The scatter in the data is presumably due to varying surface states of clays.

In all three cores from the Beaver area, there appears to be a pattern of highest zeta potential in the middle of the formation with that at the bottom being intermediate between the top and the middle, Figure 10-10. This may indicate different degrees of oxidation or rates at which the oil sand formation was deposited.

However, the absolute zeta potentials can be substantially higher than was discussed in Section 4-3-2.

10-2-6 Cation Effects

Solutions of different chloride salts containing the same chloride content but different cations were used in the measurement of zeta potential of the clay suspension. The technique was to add 3 drops of the clay suspension to 100 cc's of the solution of the chloride salt. The zeta potential measurement was then made on this suspension. The results are plotted in Figure 10-11. The blank is shown as a solid point and other symbols refer to different cations as shown in the key. It will be noted that monovalent cations initially increased the negative zeta potential of the clay, i.e. dispersion. However, higher concentrations of the salt solution resulted in lower negative zeta potentials, i.e. flocculation. Divalent cations gave lower negative zeta potentials, i.e. flocculation. Trivalent cations in low concentrations resulted in reversal of the sign from the negative to positive, but high positive zeta potentials, i.e. dispersion. With increasing concentration the positive zeta potential decreased, i.e. flocculation. Ferric ions adsorbed on clay could result in positively charged solid particles bonding to the negatively charged oil particles, and result in oil loss through mutual precipitation. This is another option for solids-oil association discussed in Section 10-2-3.

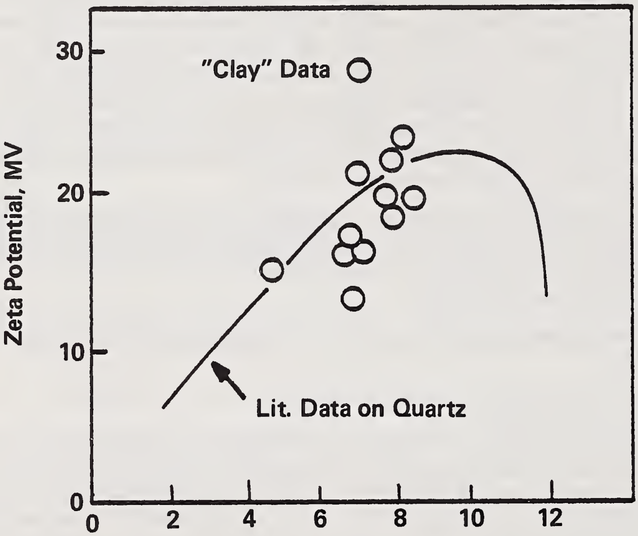
It is interesting to note that the pH did not appear to have a significant effect, and that only the type of cation plays a very important role in dispersion-flocculation and charge sign on the clay. This can be seen by comparing Fe^{++} and F^{+++} effects at low pH of ~3 that would be positive, Figure 10-9, if a cation modified clay particle was to behave similarly. However, it is evident that only low concentrations of monovalent cations are desirable to cause dispersion of the clay. This was considered to be due to polyvalent ion exchange with the sodium, an effect that is more evident with sodium tripolyphosphate that was also indicated to occur in most oil sand samples, see Section 10-2-5.

10-2-7 Anion Effects

Using the same technique, the zeta potential of clay suspension in different sodium salt solutions of different concentrations were measured. In these solutions, the sodium content was maintained constant for a given concentration. The effect of some anions used in extraction

Figure10-10

Zeta Potential and pH Data for "Clay" Samples



* pH of Diluted Suspension Used to Measure ZP MV

Beaver River

Core	Top		Hid		Bttm	
	pH*	ZP	pH	ZP	pH	ZP
15–16–2	6.7	–16.4	8.2	–19.7	7.9	–17.9
29–16–2	6.8	–16.0	7.0	–27.8	7.0	–20.7
33–14–2	7.5	–18.7	8.0	–24.2	7.8	–21.9

studies are shown in Figure 10-11. The upper plot indicates that bisulphide results in rapid flocculation at low concentrations. Sulphide and carbonate resulted in rapid deflocculation at low concentrations and flocculation with increasing concentration. The pH range of solution used is shown and no regular pattern was observed.

In the lower plot, Figure 10-11, sodium hydroxide showed a rapid flocculation with increasing concentration, whereas phosphates and silicate gave initial dispersion and the flocculation at higher salt concentrations. Tripolyphosphate and silicate appeared to cause the least flocculation of clay at high concentrations. This pattern is similar to the behavior of anions in hot water separation, see Section 7 where the use of move critical optimum caustic occurs at a lower concentration. Tripolyphosphate also gave the highest dispersion of this clay at low concentrations, although the differences between the effects of different anions are not as pronounced as those observed in studies with different cations. This was also attributed to sodium ion exchange with polyvalent ions on the clay minerals, that once in solution were effectively sequestered by the tripolyphate ion.

It should be emphasized that the eventual decline in zeta potential and hence a condition for complete agglomeration of solid and oil particles is the result of high ionic strength (as measured by specific conductance in Section 4) that collapses the double layer. Hence, this "salt effect" is not only a function of the ionic concentrations at the extremes of pH, as was discussed previously.

10-2-8 Aqueous Properties

Most workers in the general field of zeta potential have adopted the technique of adding a drop of a suspension of a given material to a diluting phase (distilled water) before zeta potential measurement. If the concept of chemical equilibrium applies, then a particle taken from its mother liquor and placed in distilled water will tend to establish a new equilibrium with its new environment. Hence zeta correlations obtained with a diluted water phase will only reflect those properties of the suspension in the mother liquor. The absolute measure of zeta potential in the separation phase is not measured by this dilution technique.

Hence, a different technique was evaluated that involved centrifuging a water phase from hot water flotation separation to remove the solids from the suspension and to obtain a clear mother liquor, to which a drop of the original suspension is then added. In this way a zeta potential of the particles of the suspension in equilibrium with the mother liquor was made. This may appear to be a very obvious and simple technique, but it does not appear to have been widely used. Further, this may be the reason why zeta potential, as measured using a dilution technique appears to be only an indicator of performance in flotation.

An example of a comparison between these two techniques is shown below:

EFFECT OF DILUTION ENVIRONMENT ON ZETA POTEMTOAL OF CLAY PARTICLES

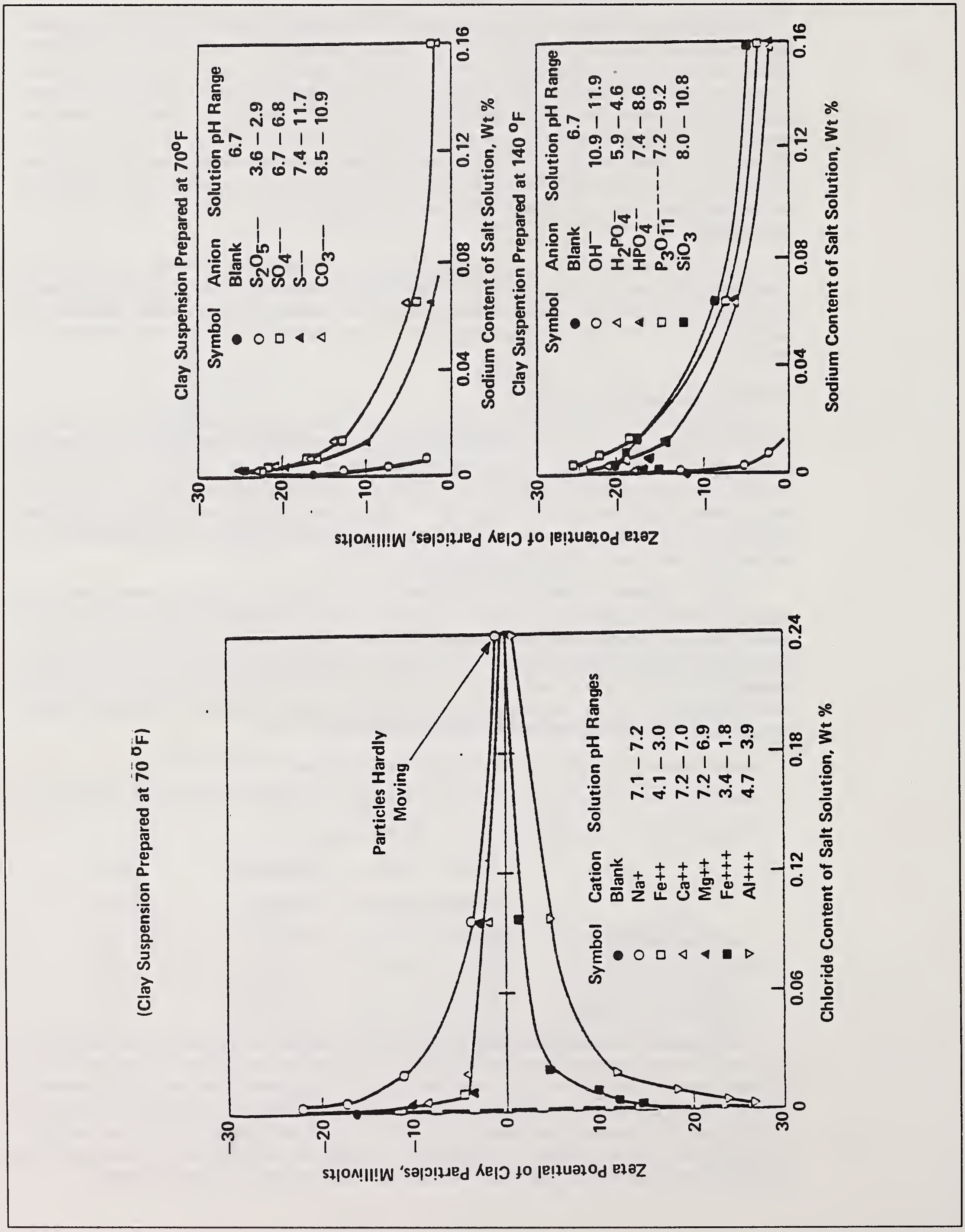
Diluting Phase:---- Distilled Water --------Mother Liquor ----

Separating Solution Used	Specific Conductance Micromhos	Zeta Potential mv	Specific Conductance Micromhos	Zeta Potential mv
NaTPP (1% Sol'n)	18	38	1400	81
NaOH (0.55% Sol'n)	28	28	6200	45

Unfortunately, because of the high salt content, the specific conductance of the solution was also high causing thermal overturn in many of the experiments, unless carried out rapidly. However, the data does show about twice the values of zeta potential for particles in the mother liquor, that is directionally consistent with typical data, see Figure 4-17. It is also consistent with the fact that zeta potential goes through a maximum and is zero at zero or high ionic strengths. The high zeta potential of fine clay particles even in diluted solutions are high and stable that points out the larger problem of water clarification and recycle in the hot water process.

Figure10-11

Cation & Anion Effect of Chloride Salts on Zeta Potential of a Clay Suspension



These substantially higher zeta potentials in actual separation will result in good separation but the more charged particles will form more stable dispersions.

Considering the details of the plot in Figure 10-12 it appears that 20 millivolts is a minimum value for the tar sands studied. This is about the threshold value (25 mv) for flocculation. The tar sands with values of this order of magnitude all exhibit poorer processability, due to acid pH and it was this observation that indicated a possible correlation of zeta potential with processability.

10-2-9 Relation to pH

Zeta potential of particles are maximized in the pH range of 8-11, Figure 10-12. Drop off is rapid at higher pH from chemical over treating. However, knowledge of both these properties is useful in understanding the behavior of different types of tar sands.

10-2-10 Specific Conductance

Unfortunately, zeta potential optima vary with specific conductance, Figure 4-19, depending on the type of oil sand and amount of additives, or total ionic strength of the water phase. Knowledge of the specific conductance is useful only to avoid large critical concentrations with a particular tar sand/chemical system, where oil recovery and zeta potential both fall off rapidly.

10-2-11 Clay Flocculation

Flocculation of clay occurs with occluded oil as a function of either acid conditions, or high ionic concentrations in the water phase. This effect results in substantially reduced oil recoveries.

10-2-12 Air Bubbles

Attempts to measure the zeta potential of very small air bubbles were unsuccessful. However, observations of the path of a rising air bubble in a field of large potential differences indicated that the sign of the charge on the bubble is negative. As this is the same sign as the negative charge, oil particles by virtue of the ionization of the naturally occurring carboxylic acid surfactants, attachment by charge does not occur. This has been observed in aeration studies in glass equipment. The cause of the tagging mechanism of air bubbles to oil particles in flotation by aeration is not known, but is thought to occur through dissolved multi-valent positive ions.

The thickness of the thin liquid film that separates a bubble resting under a silica plate submerged is a solution, was observed to be a maximum in the pH range of 8-11, where zeta potential is also maximized. This maximum hydration layer at optimum conditions for dispersion supports the concept that air-oil attachment only occurs in slurrying tar sands with water at optimum pH of ~9.5 by mechanical work performed. This provides sufficient contact for oil filming around the bubble to occur that is a major mechanism in the Hot Water Flotation Process.

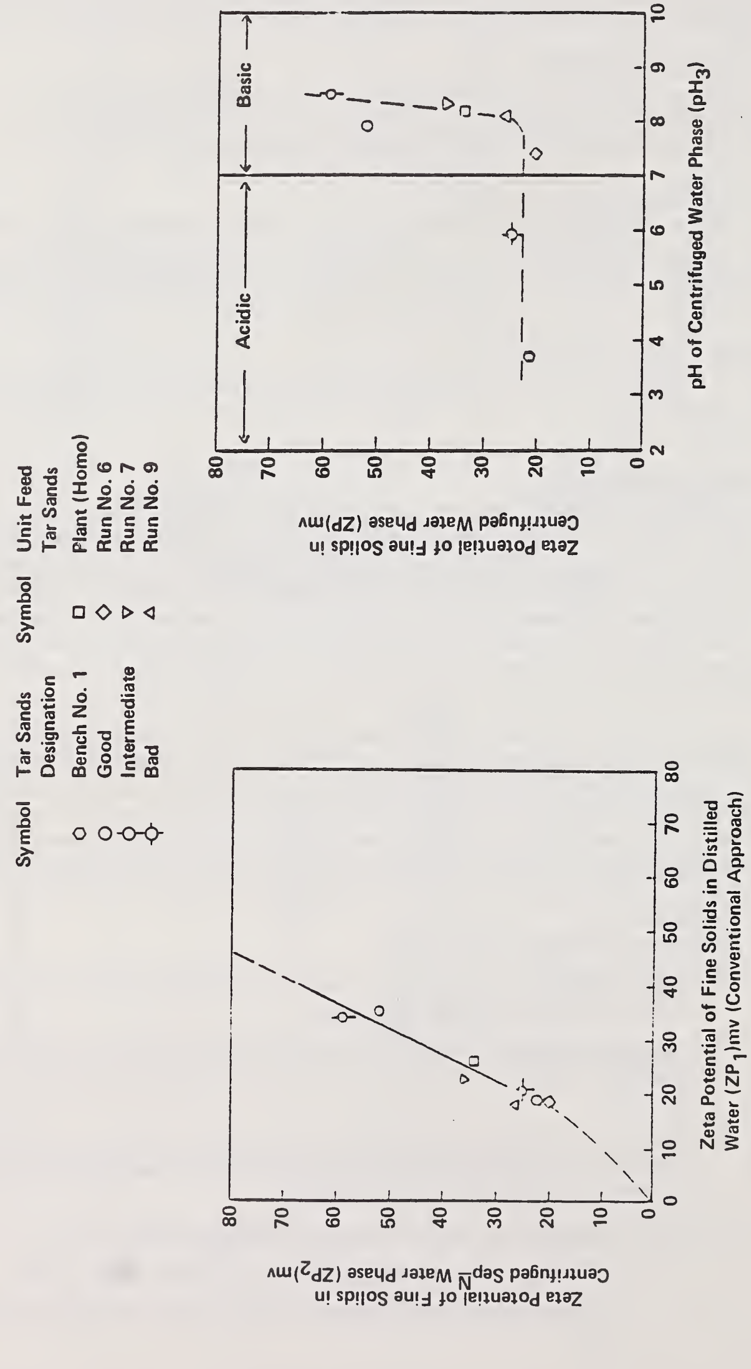
10-2-13 Summary

Some key points discussed above are:

- All particles in water suspension of benzene extracted oil and oil droplets from froth have been found to be negatively charged.
- The degree of negative charge varies with pH, passing through a maximum of alkaline conditions of about 9 pH, that is also the best conditions for separation by hot water flotation.
- The charge of oil particles suspended in solutions of varying amounts of different cations, anion (chloride) concentration being constant, has been found to be a function of the valency of the cation at low concentration,
    - *(a) Monovalent cations increase the amount of negative charge,*
    - *(b) Divalent cations decrease the amount of negative charge, and*
    - *(c) Trivalent ions reverse the sign to positive, while maintaining a high degree of charge.*

Figure10-12

Zeta Potential Relationsip of Pilot Plant Feeds



- The patterns established for benzene extracted oil and froth discussed above also apply to clay suspensions. These relationships appear to be fundamental to the components of the system.
- The addition of varying amounts of different anions, at constant cations (sodium) content, to clay suspensions have shown that certain anions (notably phosphates) at low concentration disperse the clay. At higher salt concentrations, flocculation of the clay occurs.
- Sodium hydroxide does not disperse the clay at the lowest concentrations used.
- Thus, the concentration and type of the pH additive can be critical in separations especially with low grade oil sands.

11

MICROSTRUCTURE

In the literature there appears to be some difference of opinion on the microstructure of oil sands For example, one viewpoint is that sand is surrounded by oil[1], while another viewpoint is that the oil is in the voids between the sand in the nature state; and, when disturbed in sampling or in mixing, spreads isolating the solids[2] However, to date no consistent working model of the structure of the oil sands has been presented.

As "oil sand" is variable in composition, Section 1, its structure will also vary. At least seven components should be recognized, i.e., oil, heavy minerals, sand, clays, water, gas, surface active components in the oil, and ions in the water. There are also other factors, such as particle sizes that range from large objects to colloidal particles and ions, roughness of surfaces, chemical and physical non-homogenity and non-uniformity of pores and capillaries. Although these phases and states could result in an extremely complex system of surface phenomena, with liquid-gas, liquid-liquid, solid-gas, solid-liquid interfaces permeating the whole structure, the energetics of surfaces in the previous section shows a more simple set of relationships.

Two cases of high and low grades will be considered. However, the diversity is still such that the microstructure tends to only an approximate qualitative treatment, the system being far too complex for any precise definition.

The observations, experiments and application of the principles thought to be directionally operative, are presented here to show the probable relationships of the different phases and point to the relative importance of these interfaces. The general state of undisturbed tar sands will be deduced from observations made on disturbed tar sands, as little work has been carried out directly on the formation.

---

[1] *R. Coulson, U. S. Patent 2,825,677.*

[2] *S. M. Blair, "Report on Alberta Bituminous Sand" (December 1950).*

11-1 Phase Relationships

The amounts of the various components and states of the oil sand have already been determined during the formation of the deposit, and to a much lesser extent by subsequent movement of the formation, and by mobile gases, fluids and ions in the structure.

If the relative volumes of the components are fitted together, geometrically, the sand must always touch other sand particles, leaving voids for oil and water. Liquid saturation estimates from soil mechanics both on high grade and low grade (30% fines) extracted solids indicate that the void volumes are approximately equal to the oil plus water present in the oil sands. Hence the voids can be considered as being nearly full of liquid with a small amount of gas. As was shown in Section 1, the liquid saturation declines with decreasing oil content.

Further, higher water is associated with lower grade oil sands, due to the presence of clay lenses that can support appreciable water (Section 3). The lower grade oil sands also have, in general, smaller sand particle sizes that accommodate less oil. Hence, it is postulated that the water films on these solids are probably thinner, relative to higher grades, and hence more prone to association with solids, colloidal precipitates, etc. This viewpoint is indirectly supported by the greater tendency of high grade oil sands, such as Area B, to dehydrate and oxidize.

As the sand and fines are preferentially wetted by water (Section 10-1), the solid surfaces will be hydrated with a thin film of water, and the oil will be in the spaces remaining between water over the solids.

(a) High Grades

Tar sands rich in oil are concentrated in the basinal areas, e.g. alkaline Area B tar sands. This oil is a partial continuous phase in this type of structure. Under the pressure of the formation the connate gas would be in solution in both the oil and aqueous phase as well as to a lesser extent in the voids that would have a surface film of oil. The structure envisaged is shown schematically at the top of Figure 11-1. It will be noted that the oil is in the form of tortuous threads and work has to be done to overcome the cohesion of the oil. This can be observed by pulling apart a sample of Area B tar sand.

The touching solids with their surface area covered by films of water will create a tortuous 3-dimension film systems of capillaries, through which ion can traverse the system. Capillary action by loss of water is evidenced by the immediate loss in weight of a freshly disturbed tar sands placed on a balance. As would be expected, the initial loss occurs rapidly and subsequent loss more slowly. The buildup of water droplets on the walls of a stoppered bottle or plastic bag containing a fresh sample of disturbed tar sands are other indications.

Flow of oil will be governed by particle size and temperature, so if the sand is large enough and the water content high enough (or water flow), oil separation can occur. This can be seen as small oil seepages at the face of the exposed escarpment. Further small clean sand pockets can be dug from the formation where oil has been leached. However, deep in the formation at low temperatures the oil may be regarded as a semi-solid with negative surface charges separated from the bulk of the surfaces of the solids which also carry negative charges. This relatively thick film of water has both an immobile hydration layer determined by the ions present (Section 10-2) and a mobile outer layer, in which fluid and ion movement in the structure can occur.

(b) Low Grades

When the water content is high and oil content is low, a predominating continuous water phase will exist with the oil dispersed in the interstices between the solids, bottom of Figure 11 1. Hence, the structure will be more friable. This is consistent with observations on disturbed low grade oil sand samples. For example, a lump readily crumbles between the fingers.

There will of course be intermediate systems to the two discussed where both the water and the oil are partially continuous. This occurs at about 9-10% oil content.

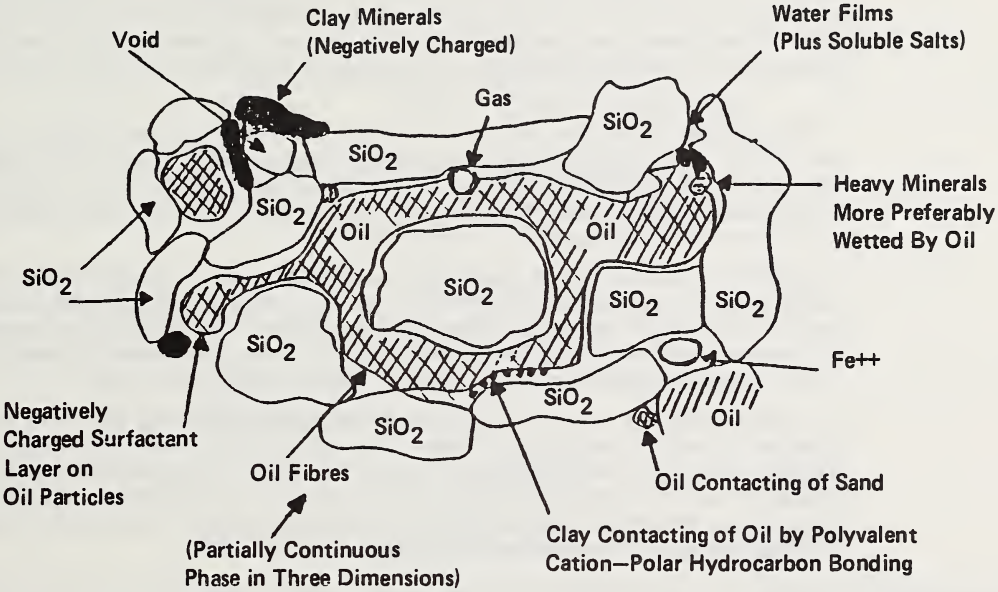
11-2 "Aging"

Most of the hypotheses on the microstructure of oil sands have been based on measurements conducted on disturbed samples. Differences will result from the process of mining the sample. These are (a) reduction in formation pressure, (b) exposure to air, and (c) division of sample.

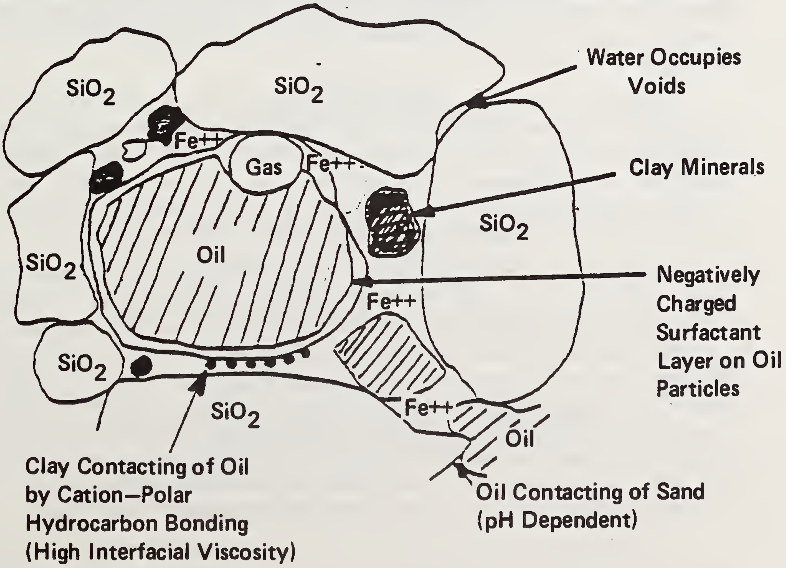
Figure11-1

Schematic Crossectional Representation of the Structure of Tar Sand (Particles are Negatively Charged)

High Grade Oil is a Predominating Continous Phase


Void
Clay Minerals (Negatively Charged)
Water Films (Plus Soluble Salts)
Gas
SiO2
SiO2
SiO2
SiO2
Oil
Oil
Heavy Minerals More Preferably Wetted By Oil
SiO2
SiO2
SiO2
SiO2
SiO2
Fe++
SiO2
Oil
SiO2
Negatively Charged Surfactant Layer on Oil Particles
Oil Fibres
(Partially Continuous Phase in Three Dimensions)
Oil Contacting of Sand
Clay Contacting of Oil by Polyvalent Cation—Polar Hydrocarbon Bonding

Water is the Predominating Continuous Phase in Low Grade


SiO2
SiO2
Water Occupies Voids
Fe++
Gas
Fe++
Clay Minerals
SiO2
SiO2
Oil
Fe++
Negatively Charged Surfactant Layer on Oil Particles
SiO2
SiO2
Fe++
Oil
Clay Contacting of Oil by Cation—Polar Hydrocarbon Bonding (High Interfacial Viscosity)
Oil Contacting of Sand (pH Dependent)

Reduction in formation pressure can result in gas coming out of solution from both oil and aqueous phases, and being lost to some extent through the structure. Interfacial oil spreading may occur during this process that can conceivably lead to some oil-solid attachment. Exposure to air can result in loss of water from the structure by three dimensional capillary action with simultaneous air penetration.

The air besides causing further oil spreading, can oxidize heavy minerals e.g. iron, sulphide, Table 11-1. This can also occur in the formation due to the introduction of air with any penetration of surface waters. The net effect of oxidation is acid generation with lowering of the natural pH and oil-solid attachment through complex formation with polyvalent ions, bitumen/solids flocculation occurs under there, Table 11-2. The steps in the mechanism are outlined in Table 11-3.

Supporting evidence for the proposed oil-solids attachment is summarized in Table 11-4 for low grade oil sands, based on several previously unrelated observations. This is also consistent with aging of oil sands that was shown in Section 4 (reproduced in Table 11-5) to raise the amount of soluble salts ten-fold. The solubilized ions (Ca, Mg, Mn, Fe) are what would be expected from dissolving of isomorphous calcites, Table 11-6.

With this type of oil sands, addition of chemicals is needed not only to adjust pH, but to sequester the polyvalent ions that go into solution in the water phase. Unfortunately, this increases the total ionic strength that causes collapse of the double layer, lowering of the zeta potential, and flocculation of oil-solids resulting in improved but still low oil recoveries. Maximum oil recovery is generally achieved at lower pH's than the optimum of 9 in these cases.

Some of the earlier oil sand samples used in these investigations were taken from or just below the exposed tar sands face at Mildred Lake, that had received much re-working, i.e., bulldozing and blasting. Further division of samples to be used in the laboratory accelerated the processes of gas and water loss, oxidation, and flocculation. Thus, the general pattern of behavior of these disturbed or "aged" tar sands will not necessarily apply to undisturbed or freshly mined oil sands that were used whenever possible.

11-3 Oxidation

The macrostructure of oil sands is a "thin film" of ~150 feet thick and near to a trillion square feet in area. This was originally a delta where the oil, presumably an "old" crude that had burst from its cap, hence resembling a young crude, was carried by rivers from its source. It was mixed with sands, silt, and clays, presumably from the Canadian Shield. This took sometime. However it is reasonable to suppose that oxidation of both heavy minerals and oil was far more prevalent and most easily achieved at the time of the formation of the deposit than during mining.

In many ways the correct interpretation of the results of research on the microstructure can add to our limited knowledge of the origin of what took place at the time of the deposit. For example, zeta potential data on cores (Section 10-2) indicated more dispersion, reflecting less oxidation in the middle zone of the formation. Hence, the central zone of the deposit may have occurred more rapidly than the top and bottom zones, assuming that the overburden is a sufficient cover to prevent subsequent oxidation later in the top marine zone.

Although, the overall poor performance in hot water flotation separation increased generally with increasing fines, *some fines are less detrimental than others* (Section 6). This high variability in behavior of fines is confusing, unless viewed as different degrees of oxidation/acid treating, that occurred from exposure and oxidation outlined above. It was clearly indicated by the lower amounts of sulphides and carbonates found in lower grade oil sands (Section 3), that appreciable oxidation appears to have occurred. This comparison is reproduced in Table 11-4 for convenience. The large amount of O_2 needed to effect these differences clearly supports the proposal that oxidation must have occurred more during the formation of the deposit. Further, the degree of oxidation and the rates needed to generate the altered state are too great to be accomplished during the time of using and handling oil sands at Mildred Lake.

Also, the rate of oxidation of the oil in laboratory oxidation tests is very slow. Yet, the zeta potential for oil particle suspensions for lower grade oil sands are higher at the same pH due to

Table 11-1

Possible Oxidation Reactions

$$\underset{\text{(Pyrites)}}{2FeS_2} + \underset{\text{(Air)}}{7O_2} + \underset{\text{(Films)}}{6H_2O} \rightarrow \underset{\text{(Migrating Fe}^{++}\text{)}}{2Fe(OH)_2} + \underset{\text{(Acid pH)}}{H_2SO_4}$$

[Hematite]

$$\underset{\text{[Siderite]}}{4FeCO_3} + O_2 + \underset{\text{[Films]}}{2H_2O} \rightarrow \underset{\text{[Geothite]}}{4FeO(OH)} + \underset{\text{(Oil Spreading)}}{4CO_2}$$

$$\underset{\text{(Ilmenite)}}{4FeOTiO_2} + 6H_2O + O_2 \rightarrow \underset{\text{[Leuoxene]}}{4TiO_2} + 4Fe(OH)_3$$

Table 11-2

Possible Acid Reactions

$$\underset{\text{(Calcite)}}{CaCO_3} + \underset{\text{(Generated)}}{H_2SO_4} \rightarrow \underset{\substack{\uparrow\downarrow \\ Ca^{++} \\ \text{(Soluble Ions)}}}{CaSO_4} + H_2O + \underset{\text{(Oil Spreading)}}{CO_2 \uparrow}$$

$$\text{[Mixed Calcites } (Ca, Mg, Mn)CO_3 \rightarrow Ca^{++} + Mg^{++} + Mn(OH)_2PPT]$$

$$Ca^{++} + Mg^{++} + (Na^+, K^+)\text{ Clays} \underset{\text{(Ion Exchange)}}{\leftrightarrow} (Ca^{++}, Mg^{++})\text{ Clays} + Na^+ + K^+$$

$$\underset{\text{(Small Size Clay and Silica)}}{Al_2Si_4O_{11} + 11H_2O} \rightarrow \underset{\text{(Colloid/PPT)}}{4Si(OH)_4 + 2Al(OH)_3}$$

Table 11-3

Mechanism of Oxidation

(1) Dehydration by capillary film thinning
(2) Air penetration of liquid unsaturation
(3) Sulphide and carbonate oxidation
(4) Generated acid dissolves carbonates
(5) Alumino-silicates (small size)
(6) Polyvalent ions diffusion in capillaries
(7) Polyvalent ions exchanged with clay surfaces
(8) Acids absorb on clays and form salts
(9) Oxygen used up slowly
(10) Lower pH established

Table 11-4

Low Oil Sand Grades Partially Oxidized during Original Formation

Components	+ More/- Less	Tentative Observations
Gas: CH_4, CO_2, N_2	-	O_2
Heavy Minerals	-	Reactive to O_2/Acid
	+	Fragmented Siderite
	+	Hematite, Geothute, Leucaxene
Solids	++	Fe Contamination Esp. Fines
Clay Lens	+	O_2 and Ion Mobilities
Water Phase	+	Polyvalent Ions: Ca, Mg
	+	Colloidal PPTS,
	-	Dispersed Clays
pH	+	Acidic
Oil Surfactants	+	Associated with Solids
	+	"Polars" in Oil Surfaces
	+	"Oxidized" Membranes: Fe
Oil	-	Adhesion

Attachment Mechanism: Solids-Polyvalent Ions-Surfactants-Oil Particle

Table 11-5

Soluble Salt Content of Tar Sands

Tar Sand Source Feed Condition	**Beaver Creek** "Fresh" (a few months)	**Hole 11** "Aged" (2 1/2 years)
Water Soluble Salts, Wt%	0.058	0.610
Major >10%	Na,Ca	Mg,Fe,Ca
Large Minor 5-10%	Al	Mn
Small Minor 1-5%	Mg,Fe,Si	Al
Large Trace <1%	Mn	Si,Na
Processability	Good	Poor
pH of Water Phase	8.0	2.5

Table 11-6

Carbonates - Heavy Minerals Cause Alkaline pH Natural Oil Sands pH 6.5 - 8.5

Pure Minerals		**Oil Sands Minerals**	
Sand	7.0	Sand	7.0
Clays		Fines	
Kaolinite	5.3	Good Area	8.4
Illite	2.9	Poor (30%)	6.9
Heavy Minerals			
Siderite	6.1		
Calcites	9.5		
Tourmaline	8.6		
Zircon	9.4		
Ilmenite	7.8		
Pyrites	5.8		

* Excludes Soluble Oil and CO_2 Effects

Table 11-7

Heavy Minerals (< 1 % >2.96 g/ml)

Inert	**Silicates**	**Oxides**
	(Nonopaques)	(Opaques)
	Tourmaline	Magnetite
	Zircon	Rutile
	Epidote	Ilmenite
	Staurolite	[Leucoxene]
	Kyanite	[Hematite]
	Chlorotoid	[Goethite]
Reactive	**Carbonates**	**Sulphides**
	Siderite	Pyrites
	Calcites*	Chalcopyrites
	Dolomite	Sphalerite

Notes: [Oxidation Products] * Isomorphous (Ca, Mg, Mn) more polar surfactants (Section 10-2). Infrared spectra confirm more "oxygenated" content, supporting oil oxidation that must also have occurred at the time of formation.

The clay strata and lenses that contain heavy minerals may be more indicative of drying up than settling, as the clay minerals generally stay suspended for substantial times, Table 11-7. Hence, local oxidation from alternate "drying up"/rewetting of these clay areas during a delta deposition is probably the cause of the variability in clay behaviour observed between high and low grade oil sands. In summary it is proposed that appreciable oxidation took place at the time of formation of the deposit. And that poor processability of low grade oil sands is the result of the chemistry changes that occured from this reaction.

11-4 Implications

This concept of the structure implies that effectively the water separation process has already taken place in nature. The Hot Water Flotation Process is therefore a physical means of separating oil from the bulk of the solids. This is best carried out on fresh oil sands, as on exposure, several phase changes, Table 11-8 can take place that decrease performance.

The major problem of separating lower grade oil sands is not one of "clay" per se, but the products of oxidation that took place at the time of the deposit, and to a lesser extent during mixing. As such, it is necessary for achieving the most efficient separation of oil to recognize what is the oil sand "state", and apply the best type of mechanical and chemical input solution for that grade. This will be discussed in more detail in Section 12.

Further, the role of clay in separating oil-sand is a function of its surface state, that is, degree of contamination with polyvalent metal ions, especially iron; and, the degree of association of oil and solids through attachment by adsorbed polyvalent metal ions. Hence, chemicals are needed to overcome this critical chemical bonding as was discussed in detail in Section 7.

11-5 General Summary

- The tar sands is a three phase complex system of several constituents involving interfacial and colloidal phenomena.
- The most probable phase relationship in tar sands (~8pH) are:
  - *Sand grains are structurally touching, and so form a continuous phase through point contacts.*
  - *Water wets the sand and hence forms a continuous phase of tortuous capillary films on the surface of the solids.*
  - *Oil can be either a continuous (>9 grade) or discontinuous (<9 grade) phase, dependent on the relative amounts of oil and water (film thickness).*
  - *Polar hydrocarbons in the oil will be oriented at the oil-water interface in the form of films (skins, membranes, etc.).*
  - *Gas will be either dissolved in the oil phase and the water phase, or exist as bubbles in the interstices surrounded by oil or by oil films (as oil spreads at a gas-water interface).*
  - *Fines, present either in lenses or in the water phase behave like water-wet sand. However, part of the fines are dispersed in the oil or are attached to oil at water interfaces.*
  - *Heavy minerals, particularly those containing titanium and zirconium, and carbonaceous fragments are associated more with the oil than with sand and clays.*
  - *Salts in solution are in equilibrium with adsorbed species or clay mineral and solid surfaces as well as heavy minerals.*
- Exposure of tar sands in sampling will result in changes in the phase relationships besides expansion such as:
  - *Gas loss by reduction in formation pressure causing oil spreading.*
  - *Water evaporation causing air introduction and oil spreading.*

  - *Oxidation of ferrous to ferric iron causing reduction in pH, reversal in the sign of the charge on particles, etc.*

All these processes contribute to poorer tar sand processability and solid-oil attachment in the structure.

- Work (shear) with water addition results mainly in the physical separation of phases, with:
  - *More work required to break down the tar sand structure when oil is a continuous phase, than when oil is a discontinuous phase.*
  - *High shear is required to affect physical separation of oil and solids.*
  - *Low temperature mixing results in oil agglomeration, and high temperature mixing results in oil dispersion and emulsification of water in oil.*
- Chemical addition to adjust pH to within the optimum range of 8-10 for separation, and to overcome solid-oil attachment results in:
  - *Increased hydration (and charge) of solid surfaces that is greater dispersion of material; oil separation; and depression of silica materials in flotation.*
  - *Ionization of naturally occurring surfactants simultaneously charging oil particle interfaces.*
  - *Precipitation of polyvalent metal ions with the anion, either from solution or adsorbed on minerals either by solubility product effects or by sequestration. Conversion of insoluble salts of carboxylic acid surfactants in the oil to sodium soaps effecting better solid-oil separation.*
  - *Reduction of amount of insoluble polyvalent metal soap formation with a corresponding emulsion reversal, i.e. , resulting in less solids and water in the froth.*

12

SEPARATIONS SUMMARY

As bitumen and solids in the tar sands are already separated in the natural state by a water film, Section 11, water separation processes, such as the Hot Water Flotation Process, are physical methods of separating a bitumen phase containing some solids and water contaminants from the bulk of the water-wet solids in the separating water phase. This general mechanism also applies to Sand Reduction as well as solvent processes provided there is enough water to form a distinct water phase containing the essentially bitumen-free separated solids.

It can be predicted from this simplified model of the oil sands structure that high bitumen recoveries are commercially possible from any process using high grade tar sands, Section 11. The degree to which these recoveries are attainable will depend on key factors being appropriately built into a plant design.

Low grade oil sands containing high levels of clay result in reduced oil recoveries from (1) Hot Water Flotation for clay contents > 5%, (2) Sand Reduction when clay contents are > 30%, (3) and solvent processes where emulsion problems and solvent-oil losses with the solids increase substantially with increasing clay content with polyvalent metal contaminated surfaces.

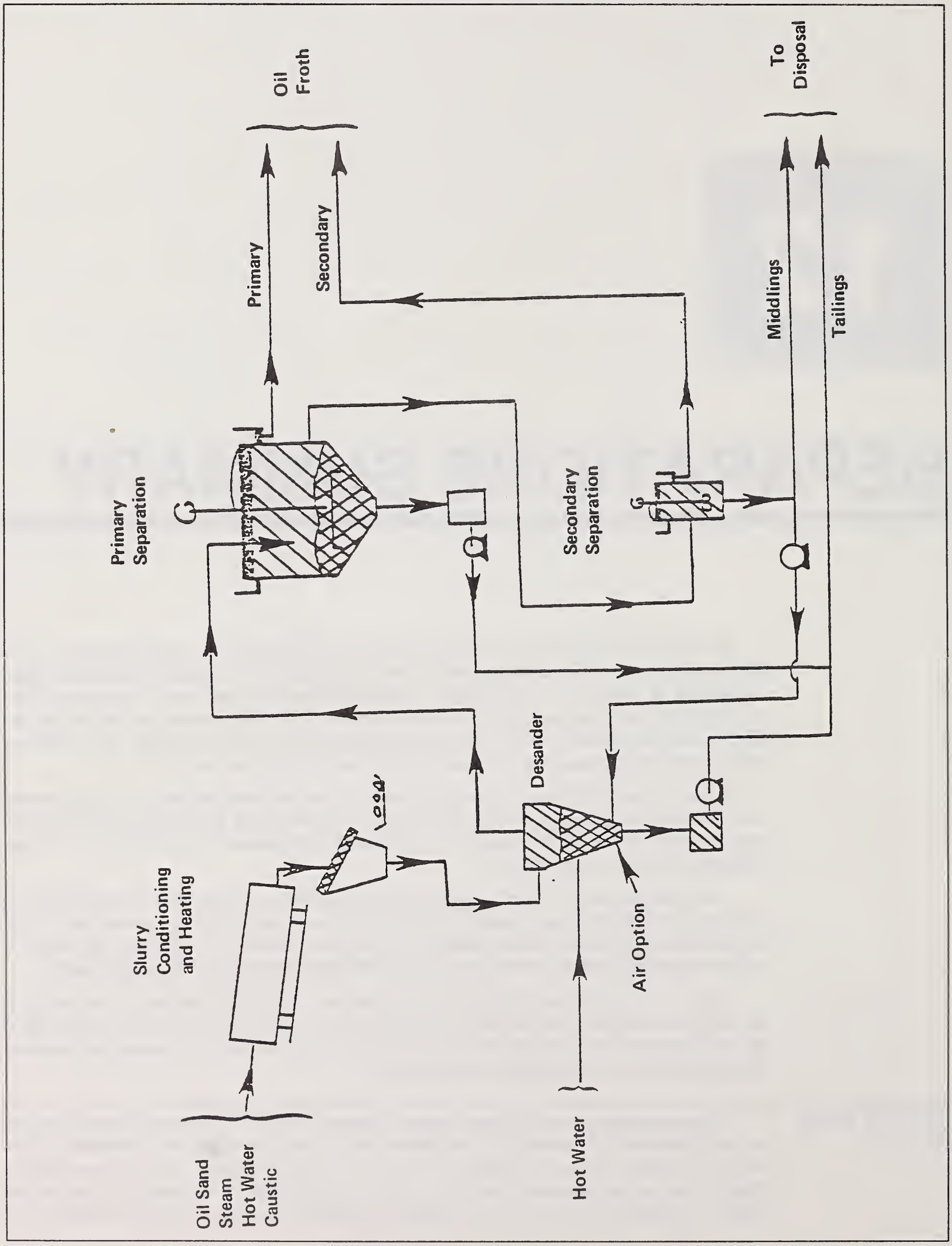
Along with the detrimental effect of clay, the degree of oxidation that has occurred either in the original formation of the oil sands or in mining and storing, are key factor contributing to poorer oil recovery. Poorer performance tar sands will require effective mechanical and chemical energy inputs for high oil recoveries to be achieved.

12-1 Oil Sand Grades

Different grades require different degrees of shear in mixing with water to breakdown the tar sand structure and disperse the components into a state where physical separation can be made. The different shear requirements are due to the relative amount of continuous bitumen phase in the tar sand structure, Section 11. This can significantly affect energy needs. For example, a low grade (<9%) tar sand will require a relatively low amount of energy to disperse tar

Figure 12-1

Tar Sand Hot Water Flotation Process



sands in water, this lower shear input may be too low and water usage may have to be reduced to increase and optimize the degree of shear to separate the oil efficiently from the sand. On the other hand, a high grade tar sand will require more shear and correspondingly more energy to break down and disperse the system. Hence, an efficient plant will be designed for the highest overall bitumen recovery from the different types of oil sand grades that will be encountered in a commercial mining site. This may not be optimum for all grades encountered, Section 6.

12-2 Hot Water Flotation

Respective studies of process variables and chemical additive effects in Hot Water Flotation separation of tar sands are discussed in Section 6 and 7. The most effective process concept from these studies is presented in Figure 12-1. Essentially, this is a scale up of the laboratory procedure. Most of the factors that influence bitumen recovery in this process sequence are summarized in Table 12-1. All of these key factors must be considered in a process design for the particular tar sand types that will be mined from a specific commercial site. Although only partial determination of these interactive effects are currently possible in the laboratory, observations of behaviour can be useful guidelines in assessing these process design factors.

12-3 Mixing (Shear)

Effective mixing is a most important process variable for achieving high primary bitumen recoveries. Essentially, new interfacial relationships are established i.e. pH, counter ions, and surface charges that affect particle dispersion.

Effective mixing is accomplished through the interaction of several factors that need to be assessed for the particular grades of tar sands from a specific mining site. These factors are (a) low energy type of mixing for slurrying the tar sands system in water, e.g. tumbler, (b) loading and water usage to optimize shear for dispersing the tar sands (c) internal to create shear and enhance occlusion of air in the slurry for attachment to bitumen, (d) mixing intensity i.e. time and rate, and (e) temperature to reduce bitumen viscosity for maximum dispersion as well as for air attachment needed in subsequent flotation of bitumen in primary separation.

12-3-1 Design

Mixing is accomplished in the laboratory by a conventional batch stirrer in a pot to create an infinite donut type spiral of movement of the tar sands slurry in hot water in the direction of mixing, Figure 12-2. Oil particle size, i.e. dispersion, can be adjusted to a large degree by the pulp density through control of water addition and feed rate. Essentially this controls the shear in the system for a fixed mixing intensity. This infinite spiral type of mixing not only disperses the components and induces shear in the system, but occludes air that can attach to dispersed bitumen particles for subsequent flotation. If the correct type of mixing is not obtained, bitumen recoveries as low as 10% have been observed instead of 90% that are characteristic of that particular oil sand. This occurs by "ride-over" of tar sands on the slurry that does not blend into the slurry and significantly affects the mechanism.

The batch mixing time is assumed to be approximately the same as the residence time in a continuous tumbler operation where a similar spiral type of mixing can be achieved commercially, Figure 12-2. Residence time or the length for a given diameter of a commercial tumbler is an important factor for optimizing the degree of mixing. It appears from laboratory separation data that the correlation is an S-shape curve. Hence residence time should be above a minimum of 4-5 minutes. However, this can also be affected by the oil sand grade.

Steam, rather than hot water heat exchange that is used in the laboratory studies, would presumably be used commercially to raise the temperature. This will be another factor in assessing the dispersion of oil and the slurry along with mixing (shear). However, hot water would be better for eliminating emulsification of steam (water) in bitumen that significantly increases bitumen viscosity and froth clean up in subsequent solvent dilution processing for removal of contaminants.

12-3-2 Conditioning

As demonstrated in previous sections, there is a characteristic curve for most of the parameters of oil sand behaviour, Figure 12-3. The optimum pH is ~9. As oil sands usually have a pH of about 7-8, the slightly more alkaline conditions of 9 pH are achieved by adding caustic

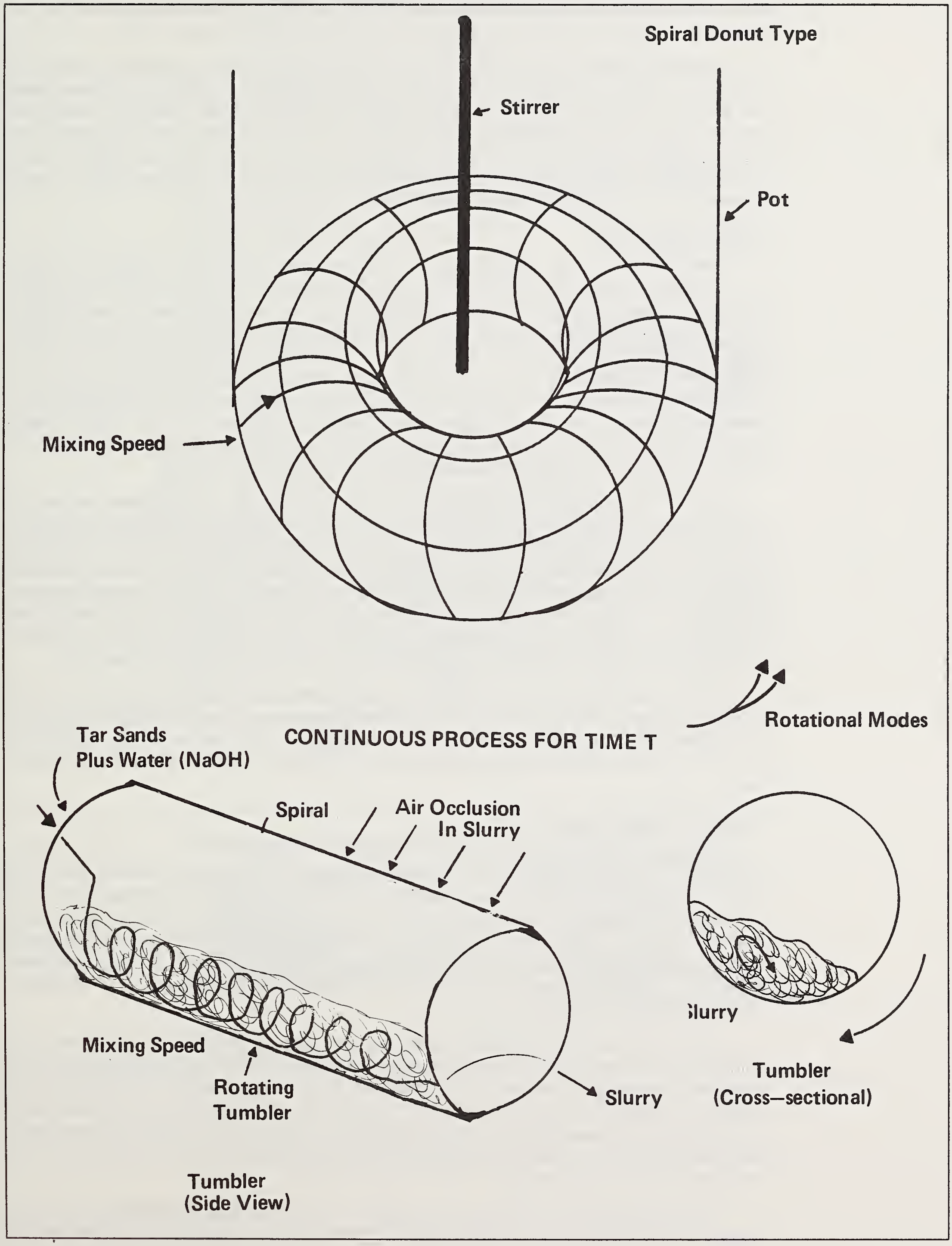
Table 12-1

Factors Influencing Flotation

Operation	Factors Controlled	 Partial Controlled	 Uncontrolled
Mixing (Tumbling)	1. Oil sand grade 2. Loading - (a) Feed rate (b) Water addition (c) Pulp density 3. Time and Intensity 4. pH and additives 5. Temperature	6. Oil particle size 7. Flocculation - Dispersion 8. Oil - Solid adhesion 9. Ion exchange Pg Ca^{++} Mg^{++} adsorption additives 10. Polar hydrocarbon dissolved in aqueous phase	11. Relative amounts of oil, sand, silts, clay and water in feed. 12. Solid particle size, shape, distribution and adsorption sites. 13. Gas occluded with oil particles. 14. pH (without additives)
Flooding - Separation [Primary]	Factors 1, 2, 4 and 5 and 15. Sand Removal 16. Froth Level 17. Settling 18. Withdrawls	Factors 6 - 10 and 19. Hydrodynamic flows 20. Separation density 21. Adjustment for grade	Factors 11 - 14 and 22. Response to variations
Flotation (Aeration) [Secondary]	Factors 1 - 5 and 23. No. of stages 24. Aeration (a) Volume (b) Intensity	Factors 6 - 10 and 25. Induction Time and attachment 26. Bubble size and path 27. Oil phase stripping 28. Solids settling or lifting	Factors 11 - 14 and 29. Gas/density 30. Response to variations

Figure 12-2

Slurrying Tar Sands with Water (Laboratory "Batch" for Time T)



soda. At this optimum pH, both bitumen recovery and froth quality are optimized by achieving the greatest dispersion i.e. maximum negative charge, of both bitumen and solids for best separation. Bulk chemical conditioning with caustic also nullifies to some extent the effects of polyvalent ions both in solution and adsorbed on clay i.e. a solubility product effect.

Only if polyvalent ions are known to be a problem either in the water phase or adsorbed on the clays in a selective mining area then other anions could be used at higher cost. These anions e.g. CO_3, $>SIO_3$, $>P_2O_5$, tend to react stoichiometrically in the system, Table 12-2. Also, when excess caustic addition is needed as well as if salts occur naturally, the higher ionic strength will tend to displace the optimum pH to lower values than 9 by reducing the surface charge. Whereas, clays either conditioned by carbonates or in the presence of carbonates appear to raise the optimum pH above 9 presumably through an ion adsorption mechanism.

12-3-3 Surfactants

In addition to inorganic effects, Table 12-2, a prime purpose of caustic addition is to ionize the carboxyl type surfactants in the interface of the oil particles. A major role of these surfactants is to facilitate oil filming and occlusion of air bubbles in slurrying. Polyvalent ions and adsorbed clays increase the interfacial viscosity and decrease the rate of filming. This increases surface charge so that discrete particles can exist due to the similarity of charge (negative) at maximum dispersion. The effect of pH on the oil particle surface charge is illustrated in Figure 12-4, and is discussed in greater detail in Section 2. This characteristic maximum curve also applies to other parameters such as oil recovery. Further, several parameter minima occur at ~9 pH, although precise definition is difficult due to several factors that cause deviations. The optimum also occurs at a breakpoint for soluble surfactants of ~500 ppm, Figures 2-4 and 2-5.

Only if the oil sands have undergone oxidation and become acid, are larger amounts of caustic required to condition the oil sands to a pH where the system can be redispersed and maximum bitumen recoveries can be achieved. These maximum bitumen recoveries are generally lower for oxidized oil sands, as acid conditioning have already developed cationic surfactants that probably are tagged directly to solids. This may be overcome in practise by specific anions, see Section 7. Further, the larger addition of caustic that will increase the ionic strength and hence reduce the optimum pH for maximum dispersion. Precise control of the optimum amount of caustic for separation is therefore difficult without prior knowledge of the tar sand "state".

Clean up of froth from oil sands that have undergone acid conditioning will also be more difficult, Section 9. The same types of carboxyl surfactants that charge the bitumen surface are also slightly soluble, Section 2, and can attach to solids that have surface adsorbed polyvalent ions. The aliphatic surfactant tails can attach to air bubbles with a classic effect of mineral flotation.

12-3-4 Air Attachment

The mechanism of bitumen flotation is illustrated in Figure 12-5. Air occluded in slurry mixing has to be compressed against oil particles for attachment to occur as surface charges are in opposition and deformation for a a certain contact time is needed for oil spreading to occur. This occurs in the tumbling action of mixing that occludes air and also causes the deformation process. Once air is attached, the bitumen can float in primary separation. Because of the opposition of surface charges between air bubbles and bitumen particles, Section 11, the air bubbles introduced in secondary flotation tend to "drag" the bitumen hydrodynamically to the surface where it can form a froth.

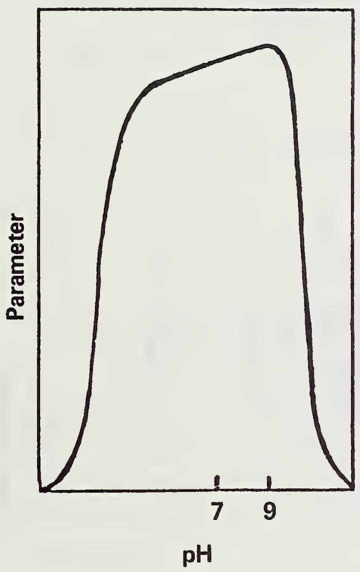
On the other hand, bitumen-solids contacting can occur as the surfactants adsorbed on the solids can line up readily with the surfactants in the surface of the bitumen resulting in solids, attachment by tagging, Figure 12-6. This attachment, however, is thought to be initiated by the presence of adsorbed polyvalent ions on the surface of the solids, as well as deformation of the oil surfaces. Hence lower energy or gentle mixing also avoids excessive solid attachment. On the other hand excessive air addition will greatly increase the solids and water contaminants of the froth from Hot Water Separation.

Some surfactants are soluble to some degree in the water phase depending upon the pH, Section 2. These surfactants can affect solids flotation readily, especially as the surfactants are

Figure12-3

Oil Sand Behaviour Relationships

(9 pH)



Oil Sand Characterization Curve

Maxima Breakpoint

- Oil Recovery
- Ionized Surfactants
- Zeta Potentials of Oil and Solids (Clays)
- Work of Adhesion

Deviations with High Conc's

- Inorganic Salts and from Oxidation
- Polyvalent Ions
- Surfactants

Also Absorbed on Clays

Minima or Breakpoint

- Contact Angles
- Surfactant Solubility
- Water Ionic Conc.
- Ca and Mg Solubilities
- Froth S/O and W/O Ratios

Figure12-4

Bitumen Particles

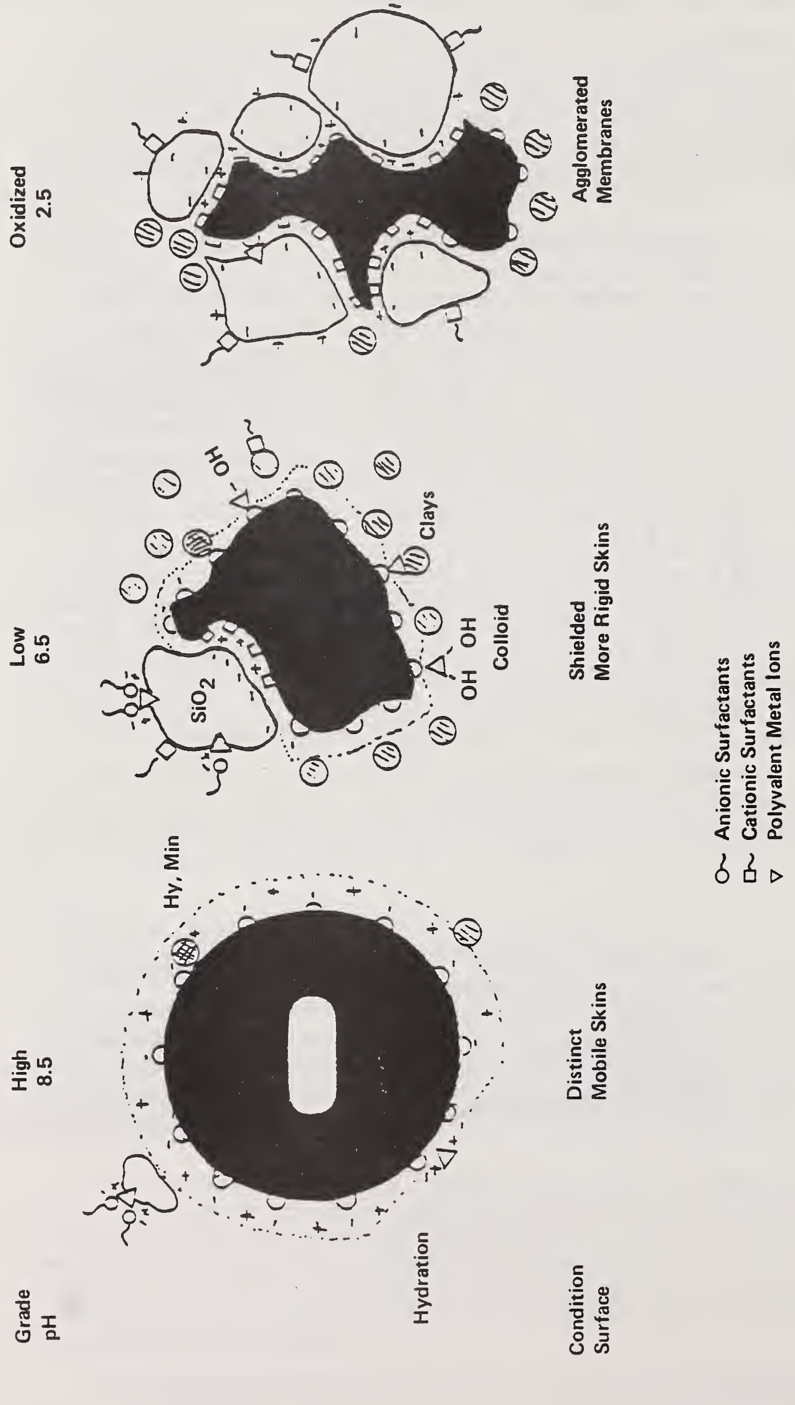


Table 12-2

Some Simplified pH Conditioning Reactions

NaOH	Neutralized Acids and Optimizes pH at 9 Disperses Solids (Practical Importance) Modifies Some Surfaces, e.g. $FeO(OH) + NaOH \leftrightarrow NaFeO_2 + H_2O$ $2NaFeO_2 + (\text{Hot})\ H_2O \rightarrow Fe_2O_3 + 2NaOH$
Na_2SiO_3	Modifies Some Sufaces and Ions $Na_2SiO_3 + 3H_2O \rightarrow \underset{\text{Deposit}}{Si(OH)_4} + 2NaOH$ $Na_2SiO_3 + Ca^{++} \rightarrow CaSiO_3 + 2Na^+$
$Na_5P_3O_{10}$	$5Ca^{++}$ (or Ca^{++} Clay) $+ 2Na_5P_3O_{10} \rightarrow \underset{\text{Sequestered}}{Ca_5(P_3O_{10})_2} + 10Na^+$

now aligned. Figure 12-6. This applies particularly in secondary flotation with an addition where the process of solids attachment and flotation can significantly affect bitumen froth quality.

As this is a critical mechanism in Hot Water Flotation, it is worth while to reiterate in summary that, air bubbles and oil particles are negatively charged and will tend to repel each other under conditions of optimum separation (pH 8-10). Oil-air attachment is therefore proposed to occur by initially electrostatic coupling of the particles by positively charged cations (induction time) followed by spreading of oil at the interface to occlude air by an oil film (after overcoming the energy barrier). Solids contaminated with natural surfactants can undergo flotation readily.

12-3-5 Clay

Clay was found to be highly detrimental in the hot water process, Section 6, by interfering with the flotation mechanism for oil recovery. An air bubble occluded into the slurry is not a sphere as supposed in Figure 12-6 but becomes elongated Figure 12-7. The leading edge in the direction of travel becomes positively charged and the trailing edge becomes negatively charged. At low clay concentrations, bitumen particles predominate and as they have high negative charges they can be adsorbed by charge neutralization at the leading edge of the elongated air bubble and they can move to the trailing edge where they can be discharged. However, spreading can also occur at the air-water interface by the filming mechanism that is so evident in oil sands, Section 10 and 11.

As clay is negatively charged, it can also compete for adsorption at the interface of the leading edge of the elongated air bubble. As the concentration of the clay increases the surface of the air bubble can be receiving and discharging clay particles that in a sense form a barrier for adsorption of bitumen. The negative clay particles tend to reduce the positive leading edge of the air bubbles. Bitumen particles are presumed to be more strongly adsorbed at the interface, so that the clay barrier although significant in reducing oil recovery does not completely exclude bitumen attachment by spreading. Further, polyvalent ions, such as ferric and aluminum, can enhance this flotation mechanism by adsorption creating a more positive air bubble surface for oil particle attachment, see Figure 10-11. There is however a time needed for this process to occur.

Figure12-5

Bitumen Flotation

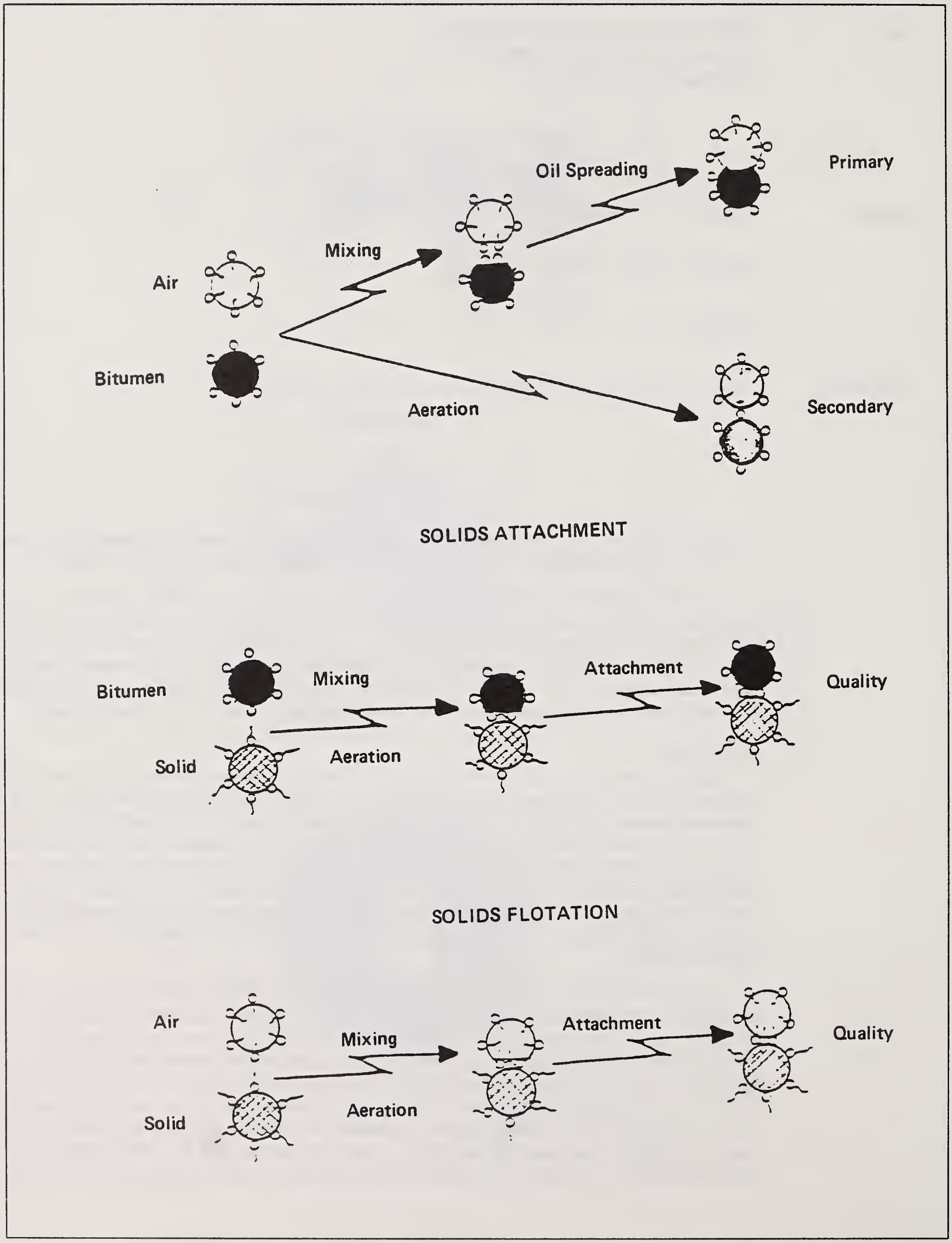
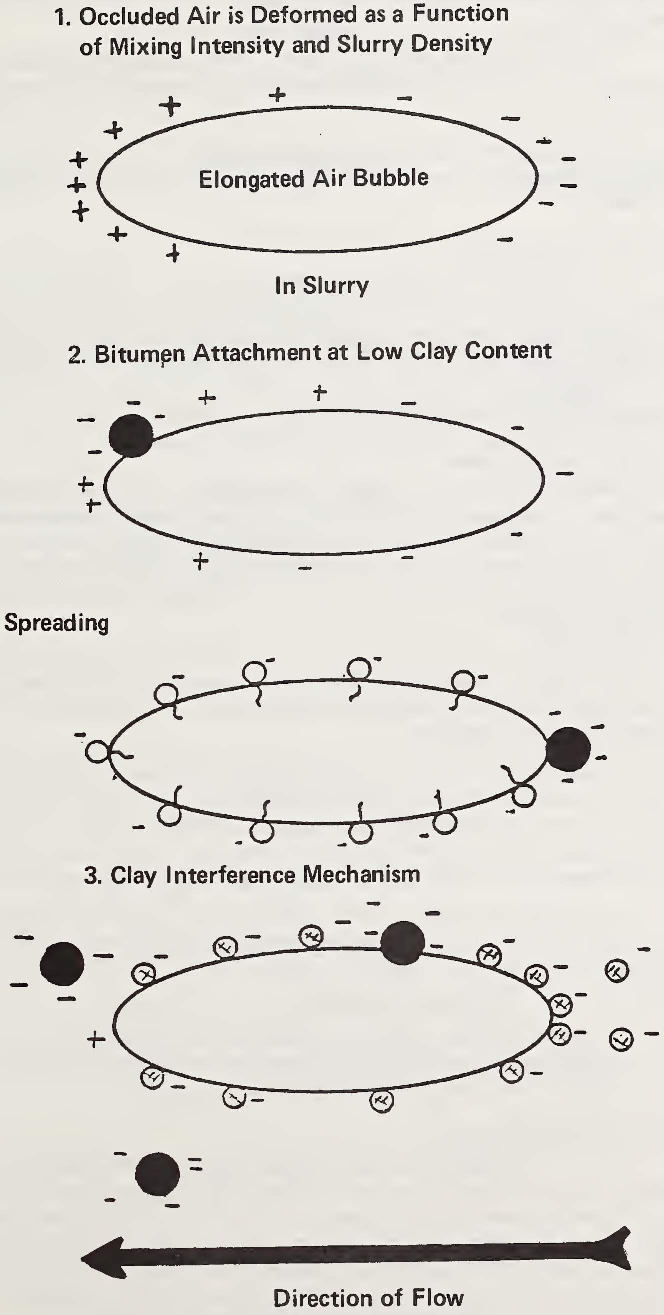


Figure12-6

Air Attachment Mechanism


1. Occluded Air is Deformed as a Function of Mixing Intensity and Slurry Density
Elongated Air Bubble
In Slurry
2. Bitumen Attachment at Low Clay Content
Spreading
3. Clay Interference Mechanism
Direction of Flow

A second detrimental mechanism of clay is due to the degree of surface contamination with polyvalent ions e.g. Fe, Ca, Mg, that cause the association of clay with the ionized surfactants on the surface of the oil particles, Section 10-2-3, forming a clay "film" on the bitumen particle surface. This results in finely dispersed oil particles that do not float and form froth. These can be observed either suspended in the water phase or more usually settled on the clean separated sand.

A third detrimental mechanism occurs when increasing amounts of clay increase the viscosity of the separating water phase that can also prevent some bitumen from floating and forming froth.

Combined, these detrimental effects of clay have a serious impact upon oil recovery and hence the economic potential for Hot Water Flotation for bitumen recovery from lower grades of tar sands.

12-3-6 Temperature

Good flotation occur within the temperature range of 140-195°F. At temperatures outside of this range, bitumen recoveries decrease rapidly. However within this range, higher temperatures of 185°F appear more optimum in effectiveness to occlude air into bitumen particles by lowering the viscosity of surface films. Further, better adhesion of oil particles in froth also appears to occur that results in higher froth quality. This seems to be more important for high grade oil sands presumably containing low API gravity oil, Section 2.

12-3-7 Lower Grades

The difficulties in processing lower grades of tar sands that have been discussed in previous sections, are summarized in Table 12-3. The basic approach in attempting to solve this problem of achieving high bitumen recoveries is to balance mixing (shear) and chemical energies, Table 12-4, while minimizing water use for proper conditioning and overcoming the problem of clays for a particular oil sand grade, Figure 1-1. As discussed in detail in Section 7, chemical type, i.e., anion, is important.

12-4 Primary Separation

The purpose of the primary separator, Figure 12-1, is to separate bitumen froth in as high yield as possible while minimizing solids and water contaminants. This is usually carried out by flooding the tar sands slurry.

Gentle stirring is conducted in laboratory separations to release entrained bitumen oil from the lower sand phase, while skimming separated froth from the surface of the water phase. This stirring movement is minimized to reduce hydrodynamic flows that can drag bitumen particles down from the metastable froth interface, with corresponding oil losses. The effect of hydrodynamic flow would probably be more pronounced in a continuing commercial operation.

As separation of froth is best achieved under quiescent conditions, one way to reduce hydrodynamic flows in the primary froth separator is to first remove the bulk of the clean sand in a prior counter-current desanding operation, Figure 12-2. This is the same concept as Sand Reduction, i.e., minimize solids handling.

The overhead water phase containing dispersed bitumen can now be separated under more ideal conditions in a secondary aeration process stage for the formation of high yields of froth containing the least amounts of contaminants.

12-4-1 Sand Removal

One of the important principles to reduce energy needs and effect better primary separations, is to minimize the handling of clean wet sand that very rapidly separates when tar sands are mixed with water. Based on results of laboratory separations, this appears to be accomplished best by countercurrent contacting the tar sands slurry with flooding water in a desanding operation that precedes the primary froth flotation cell, Figure 12-1. Stripping bitumen from the sand phase by counter-current washing with water can be further enhanced by the addition of small amounts of air distributed in the bottom of the desander.

Table 12-3

Low Grades More Difficult to Separate Efficiently

Process Observation	Relative to High Grade	Tentative Implications
Processability		
- Oil Recovery	20-90 vs. 90-99%	- Major Sep^n Problem
- Sep^n Oil Quality	More Contamination	- More Cleanup/Losses
Oil Sands		
- Oil Content	6-10 vs. 10+ %	- Mine and Process More
- State (Mixing)	Friable vs. Cohesive	- Shear Occurs in Lower Mixing but Higher Shear is Needed
- pH	7 to Acidic vs. 7 to Alkaline	- More pH Adjustment
- Solid Surfaces	More Contamination	- Inorganic Additives
- Oil Particles	Less Adhesion to Air	- Organic Additives
- Clay	Up to 35%	- Increases Density and Prevents Flotation by : Tagging to Bitumen : Reducing Bitumen/Air Attachment

Table 12-4

Treating Low Grade Tar Sands

- Identify degree of variability
- Select bulk chemical conditioning
- Balance mixing (shear) and chemical energies
  - Lower zeta potential by removing counter ions
  - Occlude/compress/decompress air for oil spreading in slurrying
- Flooding/separation establishes new counter ions, ZP and pH
- Froth: Unstable system of adhering oil particles
- Aeration: Hydrodynamic lift with electrostatic ionic attachments

Aerated bitumen from mixing is skimmed from the surface of the water phase in the primary separation as a froth. Solids underflow go to disposal. The intermediate water phase containing most of the bitumen losses due to inefficient attachment to air in mixing as well as hydrodynamic flows opposing flotation in primary separation, can be recovered from the water phase in secondary separation.

12-4-2 Froth Formation

As bitumen particles accumulate at the water surface in primary separation, they appear to be loosely attached to each other by films. However, freshly formed froth by this process can be readily redispersed by gentle agitation, although, "clumps" of bitumen particles are observed, indicating that some coalescence also occurs in froth formation. Hence, froth is an metastable system of adhering bitumen particles. The quality of froth also decreases with poorer grades as illustrated in the example in Figure 12-7, that implies a need for flexibility in solvent dilution clean up, see Section 9.

Although it is difficult to verify in small laboratory experiments, froth is visualized to form as a vertically graded phase from condensed clumps of bitumen particles at the top presumably with smaller drainage channels, to bitumen particles loosely held together by films in the water interface at the bottom of the froth layer. Entrained water wet solids are mostly in the water channels, as well as "tagged" to the bitumen particles surfaces, via polyvalent ion. Higher temperatures of 185°F are probably best for accelerating the particle attachment and coalescence mechanism proposed above.

12-5 Secondary Separation

In general, high oil recoveries of >90% can be achieved with most tar sands in a two stage froth recovery process, Figure 12-2. Most of the unrecovered bitumen particles from the primary separation are dispersed in the water phase, that can be treated with mechanically dispersed air in secondary separation to complete the process of bitumen recovery, Figure 12-8. In this case, the mechanism appears to be more of a hydrodynamic lift for bitumen particles from electrostatic and ionic attachments rather than oil spreading. Hence, careful design for good air dispersion and distribution of fine bubbles is important.

In general, the smaller the bubble size and the longer the bubble path from the swirling action of stirring in the aeration cell, are key factors for obtaining high secondary bitumen recoveries. The upper limit of secondary oil recovery for a specific preconditioning of a tar sand grade is quite rapidly achieved. However, a penalty has to be paid for achieving high oil recoveries in a larger amount of solids and water contaminants in the froth that have to be subsequently removed in froth clean up by solvent dilution and chemical treatment. Flotation of solids, as discussed before and water emulsification in bitumen are main causes of the higher contaminants in the secondary froth.

12-6 Sand Reduction

The concept of Sand Reduction is to remove with minimum handling the bulk of clean water wet solids that separate on mixing tar sands with cold water from the bitumen that is virtually completely concentrated in agglomerates. The low temperature agglomeration mechanism is distinctly different from the high temperature flotation mechanism discussed above, see also Section 8.

The process is simple and appears to be able to tolerate clay. Low grade tar sands can be processed for high bitumen recoveries in admixture with high grade tar sands. Contaminant removal from bitumen agglomerates can be readily achieved by solvent dilution, Section 9. This process has many potential advantages over Hot Water Separation.

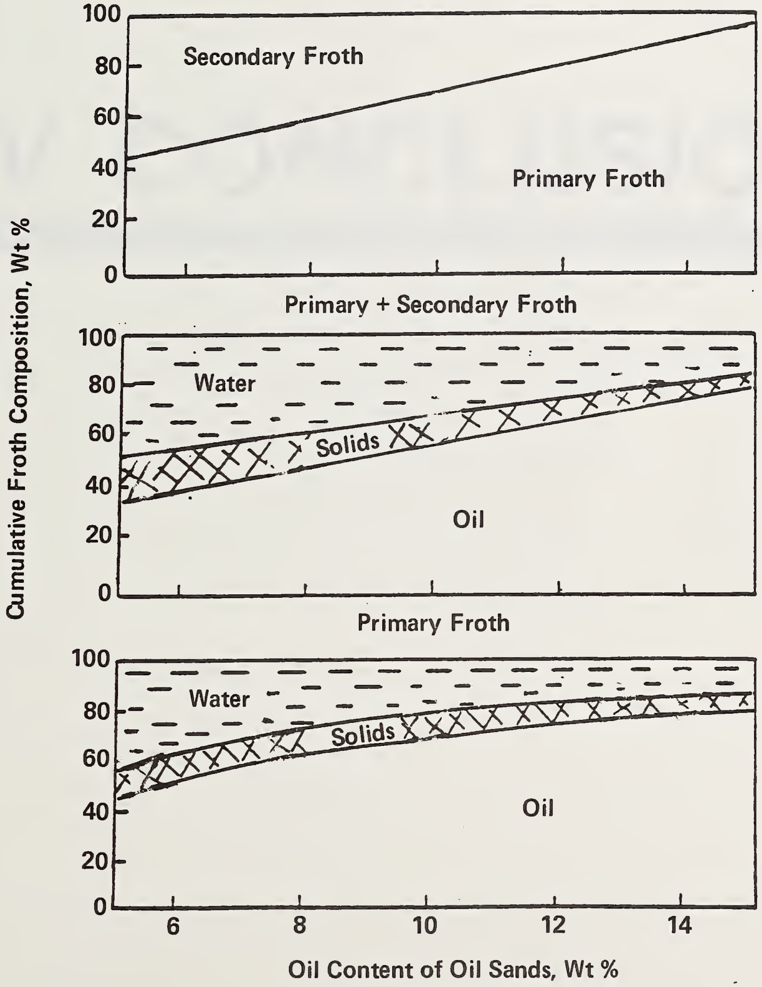
12-7 Solvent Processes

In general, solvent dilution processes, e.g. Royalite Process in 1957, that reduce the viscosity of the bitumen phase have not been successful due to emulsions and high solvent-bitumen losses in the separated solids phase.

Solvent dilution processing, however, is effective for contaminant removal from froth and agglomerates. Emulsion problems, that vary as a function of tar sand grade, can be overcome by either chemical treatment and centrifuging or in a probably more efficient gravity settling-centrifuging separation process discussed in Section 9.

Figure 12-7

More Contaminant Removal Needed with Poorer Oil Sands



IV. CONCLUSION

CONCLUSION

A perception of the nature of oil sands and of its behaviour in separation was achieved from these studies that forms a basis on which more efficient operation and process control can be devised, as well as more effective processes can be developed.

The specific conclusions contained within the individual sections are considered to be valid only within the context of the conditions and types of tar sands studied. Further investigations are needed to verify the validity of some of the more specific findings with a wider variety of tar sands, and in larger scale operations.

The tar sands still remains a challenge to our understanding.

V. APPENDICES

Data tables of separations, not necessarily discussed in the text, are included in the following Appendix Sections for completeness and reference. It should be noted that tar sand samples were taken from several locations and had undergone various degrees of aging. Hence, results should be suspect and used only as a basis for further experimentation with fresh tar sands. Also, a listing of the experimental procedures used at the time is included, as these techniques determine the quality and precision of the data generation, and hence the mechanisms proposed.

V1

HOT WATER FLOTATION PARAMETERS

V1-Table 1

Studies on the Effects of Water in Mixing, Mixing Intensity and Mixing Time with a "HighWater" Area B Tar Sand

Tar Sand feed as received was like a paste and contained 13.3 Wt % water, 10.7 Wt % oil, 6 Wt % 325-fines, and 71 Wt % sand constant conditions were 160^{o}F in mixing and separation, 2 aerations at 2.0 cubic feet/hour for 5 minutes.

Effect	---Water in Mixing---						---Mixing Intensity---			---Mixing Time---		
Conditions												
Mixing: Time, min	5						5			5	10	15
Speed, rpm(1)	120						120	240	240	120		
In Sep^n: Speed, rpm(2)	120						120	120	240	120		
Water in mixing, wt %(3)	0	5	10	15	20	30	15			15		
Water in sep^n, Wt %(4)	80	75	70	65	60	50	65			65		
Froth Composition, Wt %												
Water	26.9	22.8	29.5	26.6	26.6	21.7	26.6	30.9	35.8	26.6	29.6	35.8
Solids	18.6	21.3	21.1	19.7	19.8	20.8	19.7	21.9	20.6	19.7	21.6	22.4
Oil	54.5	55.9	49.4	53.7	53.6	57.5	53.7	47.2	43.6	53.7	48.8	41.8
Solids to Oil Ratio	0.34	0.38	0.43	0.37	0.37	0.36	0.37	0.46	0.47	0.37	0.44	0.54
Yields, Wt % (Water Free Basis)												
Froth	17.2	17.1	16.8	16.0	15.5	17.5	16.0	17.8	17.8	16.0	16.8	17.2
Water Phase	5.2	5.2	5.2	4.8	6.2	5.3	4.8	5.1	5.8	4.8	4.5	4.9
Sand	77.6	77.7	77.9	79.2	78.4	77.2	79.2	77.1	76.4	79.2	78.7	76.8
Oil Recovery, Wt %, in (output)												
Froth	97.4	97.5	96.5	96.1	95.0	96.4	96.1	98.7	99.35	96.1	97.8	98.8
Water Phase	1.95	1.8	2.6	2.5	3.8	1.6	2.5	1.1	0.59	2.5	1.4	0.0
Sand	0.65	0.7	0.9	1.4	1.2	2.0	1.4	0.2	0.06	1.4	0.8	1.2
Tar Sand Composition, Wt % (Cal^c)												
Oil(5)	11.5	11.05	10.5	10.5	10.1	11.6	10.5	10.8	10.5	10.5	10.4	10.0
Water(6)	12.8	12.85	14.4	13.6	15.7	13.3	13.6	12.5	13.2	13.6	12.6	11.6
Fines(7)	8.0	8.4	8.5	7.6	8.3	8.4	7.6	9.3	10.0	7.6	8.3	10.6
Sand	67.7	67.7	66.6	68.3	65.9	66.7	68.3	67.4	66.3	68.3	68.3	67.8

(1) Revolutions of three bladed paddle.
(2) Stirrer speed in flooding-aeration.
(3) Water added based on tar sand does not include water in tar sand.
(4) Water added in flooding.
(5) Grams of oil recovered, wt %.
(6) 100 - (grams of oil and solids recovered).
(7) Solids recovered in froth and water phase.

V1-Table 2

Effect of Low Addition in Mixing with and without Air in Subsequent Separation Aged, Area B Tar Sand

Feed: A sample of Area B Tar Sands (18 months storage at atmospheric temperatures and 2 weeks at 70-80°F) contained 2.5% water, 13.5% oil, and 84.0% solids, conditions:

Conditions								
Water in: Mixing	5	10	20	30	5	10	20	30
Flooding	75	70	60	50	75	70	60	50
Slurry Rating(1)	A	A	B	C	A	A	B	C
Air Rate, Cubic Ft/Hr	0.0				2.0			
Results, Wt %								
Froth Composition								
Water	28.3	31.8	39.4	33.1	32.0	34.6	43.1	39.6
Solids	37.2	26.7	22.2	24.2	27.7	29.6	24.0	28.2
Oil	34.5	41.5	38.4	42.7	40.3	35.8	32.9	32.2
Solids/Oil Ratio	1.08	0.65	0.58	0.57	0.69	0.83	0.73	0.87
% Wet Froth from 1st Aeration	85	90	90	88	64	61	66	63
Yields (Water Free Basis)								
Froth	9.6	7.8	7.2	7.1	13.4	12.7	10.8	14.0
Water Phase	6.4	7.6	8.8	5.5	7.5	7.6	9.4	6.8
Sand	84.0	84.6	84.0	87.4	79.1	79.7	79.8	79.2
Oil Recoveries (Output)								
Froth	34.3	33.3	32.4	32.7	57.9	50.0	44.9(2)	54.5
Water Phase	27.5	30.3	40.5	21.5	29.1	30.3	34.8	28.0
Sand	38.2	36.4	27.1	45.8	13.0	19.7	20.3	17.5
Tar Sand Composition (Cal^{c})								
Oil(3)	13.0	13.6	13.6	13.3	13.1	13.3	13.3	13.2
Water	4.0	3.7	3.5	3.9	3.7	3.8	4.2	3.8
Fines	7.3	6.1	5.6	4.9	8.7	8.8	8.8	9.2
Sand	75.7	76.6	77.3	77.9	74.5	74.1	73.7	73.8

(1) Slurry in mixing was either (A) not enough water - mix tumbled - occluding air or (B) hardly enough water for a good slurry - mix tumbled - occluding air or (C) good slurry.

(2) Low - only with poor quality Area B type Tar Sands, some oil spirals around stirrer and fragment losses to sand and water phase lowers oil recovery.

(3) Grams of oil recovered, wt %.

(4) 100 - (grams of oil and solids recovered).

(5) Solids recovered in froth and water phase.

V1-Table 3

Studies on the Effects of Water in Mixing, Mixing Intensity and Mixing Time with an Area D Tar Sand

Tar Sand feed contained 3.5 Wt % water, 9.5 Wt % oil, 6.0 Wt % 325-fines, and 81.0 Wt % sand. Constant conditions were 160°F in mixing and separation, 3 aerations at 0.5 cubic feet/hour.

Effect	**Water in Mixing**			**Mixing Intensity**		**Mixing Time**		
Conditions								
Mixing time, min	5			5		15	5	15
speed, rpm(1)	120			120	240	120	240	
In sep^n, speed, rpm(2)	120			0	240	120	240	
Water in mixing Wt %	15	20	60	30		30		
Water in Sep^n, Wt %	65	60	20	50		50		
Results, Wt %								
Froth Composition								
Water(3)		53.7	51.1	51.4	54.3	53.2	54.3	54.0
Solids		19.9	18.6	20.8	26.1	16.8	26.1	24.0
Oil		26.4	30.3	27.8	19.6	30.0	19.6	22.0
Solids/oil ratio		0.75	0.61	0.75	1.33	0.56	1.33	1.09
Yields (water free basis)								
Froth		14.6	13.7	8.4	21.9	14.0	21.9	21.3
Water phase		4.3	4.6	7.4	3.0	3.9	3.0	2.6
Sand		81.1	81.7	84.2	75.1	82.1	75.1	76.1
Oil Recoveries								
1st and 2nd Froths		82.6	81.0	42.5	90.9	89.9	90.9	95.6
Total froth		87.3	88.1	51.6	96.9	92.1	96.9	98.8
Water phase		7.5	8.7	33.0	1.6	4.3	1.6	0.3
Sand		5.2	3.2	15.4	1.5	3.6	1.5	1.0
Tar Sand Composition (Cal^c)								
Oil(4)		9.2	9.3	9.0	9.3	9.4	9.3	9.9
Water(5)		3.8	3.8	3.9	4.0	3.7	4.0	3.3
Fines(6)		9.5	8.6	7.6	14.7	8.3	14.7	13.2
Sand		77.5	78.3	79.5	72.0	78.7	72.0	73.5

(1) Revolutions of three bladed paddle.
(2) Stirrer speed, and water added in flooding - aeration and skimming.
(3) Water is slightly higher than usual could have resulted from multi-skimming employed.
(4) Grams of oil recovered Wt %.
(5) 100 - (grams of oil and solids recovered).
(6) Solids recovered in froth and water phase.

V1-Table 4

Effect of Low Water Additions in Mixing on an Area D, Hole 4, Tar Sand with and without Air in Subsequent Separation

Feed: A sample of Area D, Hole 4, (9 month cold storage at 40°F and 1 months storage at 70-80°F) contained 3.5% water, 9.1% oil, and 87.4% solids. Feed was difficult to homogenize due to clay and lumps.

Conditions								
Water in: Mixing	5	10	20	30	5	10	20	30
Flooding	75	70	60	50	75	75	60	50
Slurry Rating[1]	A	A	B	C	A	A	B	C
Air Rate, Cubic Ft/Hr	0.0				2.0			
Results, Wt %								
Froth Composition								
Water	44.3	47.2	49.3	44.4	53.0	55.5	53.6	50.2
Solids	19.0	19.3	14.1	18.0	23.2	21.7	21.5	24.4
Oil	36.7	33.5	26.6	37.6	23.8	22.8	24.9	25.4
Solids/Oil Ratio	0.52	0.58	0.53	0.48	0.97	0.95	0.87	0.96
% Wet Froth from 1st Aeration	100	98	99	100	57	54	46	62
Yields (Water Free Basis)								
Froth	1.2	1.7	1.0	1.1	8.3	8.2	9.5	10.6
Water Phase	12.9	13.9	15.9	15.2	11.7	12.3	11.6	10.6
Sand	85.9	84.4	83.1	83.7	80.0	79.5	78.8	78.8
Oil Recoveries (Output)								
Froth	9.3	10.8	6.8	7.5	45.1	47.6	58.5	60.2
Water Phase	57.2	64.0	71.5	75.4	43.4	44.2	34.8	30.7
Sand	33.5	25.2	21.7	17.1	11.5	8.2	6.7	9.1
Tar Sand Composition (Cal^{c})								
Oil[2]	8.5	9.2	8.9	9.1	9.0	8.5	8.5	8.7
Water[3]	4.0	4.2	5.0	5.0	3.7	4.4	3.2	3.3
Fines	7.9	8.0	9.1	7.8	11.2	11.8	12.6	12.6
Sand	79.6	78.6	77.0	78.1	76.1	75.3	75.7	75.4

(1) Slurry in mixing was either (A) not enough water - mix tumbled - occluding air or (B) hardly enough water for a good slurry - mix tumbled - occluding air or (C) good slurry.

(2) Grams of oil recovered, Wt %.

(3) 100 - (grams of oil and solids recovered).

(4) Solids recovered in froth and water phase.

V1-Table 5

Effect of Minimum Slurry(1) and Standard Water Additions in Mixing on Fresh Spot Samples of Area B, and Area Holes 9 and 11 Tar Sands

Feeds: Area B tar sand contained 12.8% oil, 11.5% water and 75.7% solids.
Area D, Hole 9, contained 10.1% oil, 3.2% water and 86.7% solids.
Area D, Hole 11, contained 8.6% oil, 4.0% water and 87.4% solids.

Tar Sand Area (Hole No.)	B		D(9)		D(11)	
Water in Mixing/Flooding	5/75	30/50	15/65	30/50	15/65	30/50
Results, Wt %	No Air					
Froth Composition						
Water	22.8	22.5	50.0	38.7	86.3	62.1
Solids	10.1	6.7	7.9	4.6	11.2	13.0
Oil	67.1	70.8	42.1	56.7	2.5	24.9
Solids/Oil Ratio	0.15	0.10	0.19	0.08	4.41	0.52
% Net Froth from 1st Aeration	93	92	91	82		
Yields (water free basis)						
Froth	16.6	15.4	10.2	8.3	0.8	1.9
Water Phase	2.4	2.1	5.0	4.7	15.4	13.9
Sand	81.0	82.5	84.8	87.0	82.8	84.2
Oil Recoveries in (output)						
Froth	99.5	98.7	70.5	74.4	1.8	14.4
Water Phase	0.5	1.3	26.5	22.0	83.6	67.3
Sand	0.0	0.0	3.0	3.6	14.6	18.3
Tar Sand Composition (Cal^{c})						
Oil(2)	12.9	13.0	10.2	10.0	8.4	8.3
Water(3)	11.3	9.4	3.3	3.5	5.8	5.4
Fines(4)	4.0	2.9	4.8	2.9	9.1	8.1
Sand	71.8	74.7	81.7	83.6	76.7	78.2

(1) Enough water to form an homogeneous mixture.
(2) Grams of oil recovered, Wt %.
(3) 100 - (grams of oil and solids recovered).
(4) Solids recovered in froth and water phase.

V1-Table 6

Effect of Aeration Time, Rate, Frequency, Water Addition, and Tar Sand Charge with an Area D, Hole 10 Tar Sand

Feed: A sample of Area D, Hole 10, contained 4.6% water, 11.6% oil, and 83.9% solids.

Experiment No. **Conditions**	1	2	3	4	5	6	7	8
Tar sand charge, grams	100	100	100	100	100	100	50	200
Water in mixing/flooding, grams	30/50	30/50	30/50	30/130	30/50	30/130	15/25	60/65
No. of aerations	1	2	1	2	1	1	2	2
Aeration time, min	5	5/5	10	5/5	20	20	5/5	5/5
Air rate, cubic Ft/Hr	2.0	2.0	2.0	2.0	0.5	0.5	2.0	2.0
Relative Total Air	1	2	2	2	1	1	2	2
Results, Wt %								
Total Froth Composition								
Water	40.9	45.6	42.0	43.2	45.8	38.2	39.5	40.3
Solids	5.6	6.1	6.1	5.7	5.2	4.9	14.5	11.0
Oil	53.5	48.3	51.9	51.1	49.0	56.9	46.0	48.7
Solids/Oil Ratio	0.11	0.13	0.12	0.11	0.11	0.09	0.32	0.23
% Wet Froth from 1st Aeration	100	55	100	61	100	100	53	58
Yields (Water Free Basis)								
Froth	7.1	10.8	7.5	12.2	5.0	6.2	13.0	2.9
Water Phase	7.1	4.5	7.1	3.5	8.8	7.9	4.0	6.0
Sand	85.8	84.7	85.4	84.3	86.2	85.9	83.0	91.1
Oil Recoveries in (Output)								
Froth	53.8	78.8	57.5	88.2	39.1	48.6	84.3	20.5
Water Phase	42.6	18.3	40.0	10.6	57.1	48.5	13.7	35.8
Sand	3.5	2.9	2.5	1.2	3.8	2.9	2.0	43
Tar Sand Composition (Cal^c)								
Oil(1)	11.2	11.5	11.1	11.8	11.0	11.1	11.2	11.1
Water(2)	5.5	5.1	5.4	4.8	5.6	5.5	4.7	5.4
Fines(3)	2.6	3.3	3.0	3.3	2.5	2.6	5.2	2.2
Sand	80.7	80.1	80.5	80.3	80.9	80.8	78.9	81.3

(1) Grams of oil recovered, Wt %.
(2) 100 - (Grams of oil and solids recovered).
(3) Solids recovered in froth and water phase.

V1-Table 7

Cold Slurrying Tar Sands with Water prior to Dense Phase Separation Gave Higher Oil Recoveries and Cleaner Sand

Tar Sand	**Area D, Hole 9**					**Area D, Hole 10**				
Experiment	**Tar Sand Blank**		**Slurry**			**Tar Sand Blank**		**Slurry**		
			1	**2**	**3**			**4**	**5**	**6**
			Cold Mixing Pretreatment(1)(2)							
Sample Time, Hours	-	0.0	0.05	1.0	3.0	-	0.0	0.05	1.0	3.0
Slurry: Water, Wt %	-	-	28.3	27.7	26.6	-	-	27.8	27.2	26.6
Temperature, °F	-	-	88	94	95	-	-	78(5)	82(5)	
lb/hour	-	-	2300			-	-	2400		
			Dense Phase Separation(3)							
Results, Wt %										
Froth Composition										
Water	-	47.0	48.2	44.2	51.9	-	39.8	36.7	37.4	36.7
Solids	-	19.4	16.3	16.6	16.5	-	13.2	14.3	14.6	16.6
Oil	-	33.6	35.5	39.2	31.6	-	47.0	49.0	48.0	46.7
Solids/Oil Ratio	-	0.58	0.46	0.43	0.52	-	0.28	0.29	0.30	0.3
Wet Froth From										
First Aeration	-	78	71	75	73	-	63	93	92	94
Second Aeration	-	22	29	25	27	-	37	7	8	6
Yields (Water Free Basis)										
Froth	-	13.6	13.9	13.0	13.0	-	12.4	11.2	10.7	11.3
Water Phase	-	5.3	7.8	6.9	6.6	-	2.1	2.3	2.5	2.6
Sand	-	81.1	78.3	80.1	80.4	-	85.5	86.5	86.8	86.1
Oil Recovery In (Output)										
Froth	-	89.3	90.1	94.5	99.4	-	97.2	99.1	99.4	99.5
Water Phase	-	7.6	9.9	5.6	0.6	-	1.4	0.7	0.6	0.5
Sand	-	3.1	0.0	0.0	0.0	-	1.4	0.2	0.0	0.0
Feed Composition (Cal^{c})										
Oil	9.6	9.2	7.7	7.1	6.2	11.8	11.6	8.1	7.7	8.1
Water	3.4	5.2	27.3	26.6	27.6	4.5	5.5	26.4	26.4	25.6
Fines	87.0	9.0	8.1	7.5	8.0	83.7	5.0	3.9	4.0	4.7
Sand	87.0	76.6	56.9	58.8	58.2	83.7	77.9	61.6	61.9	61.6
On A Dry Basis(4)										
Oil	-	9.6	10.5	9.7	8.6	-	12.3	10.9	10.5	10.9

(1) See Memorandum R 6571, on An Evaluation of the Pumping Characteristics of an Intermeshing Worm Feeder. Our File 9-21 by C.W. Bowman.

(2) With Hole 9 the equipment configuration had three 90° bends in the return line, whereas with Hole 10 60° bends gave a return loop of lower resistance to flow.

(3) Using a preliminary procedure, Memorandum No. 14, Coarse Brass Filter. No water addition in mixing, and 50 wt % on tar sand in flooding.

(4) Variations could have resulted from sampling as oil was continually breaking off the walls of the equipment, or from the higher temperature effecting more plating out of oil.

(5) Controlled by cooling with ice.

V1-Table 8

Effect of Air Rate on Oil Recovery and Froth Composition for a Good Quality Tar Sand - Area B

Feed: A sample of Area B contained 11.3% oil, 0.6% water and 88.1% solids.

Air Rate, cubic feet per hour	0.0	0.1	0.2	0.5	2.0	3.5
Results, Wt %						
Froth Composition						
Water	42.5	39.8	35.5	34.2	33.3	28.8
Solids	10.6	16.9	14.6	17.2	16.4	17.3
Oil	46.9	43.2	49.9	48.6	50.4	53.9
Solids to Oil Ratio	0.23	0.39	0.29	0.35	0.33	0.32
% Wet Froth from 1st Aeration	82	82	80	79	89	93
Yields (Water Free Basis)						
Froth	11.4	14.5	14.5	15.3	14.9	15.6
Water Phase	2.6	2.3	1.9	1.9	1.7	1.6
Sand	86.0	83.3	83.7	82.8	83.4	82.8
Oil Recoveries in (output)						
Froth	82.7	91.4	95.3	95.3	96.4	97.3
Water Phase	6.3	3.6	2.9	2.9	2.0	1.7
Sand	11.0	5.0	1.8	1.8	1.6	1.0
Tar Sand Composition (cal^{c})						
Oil(1)	11.3	11.4	11.8	11.9	11.5	12.1
Water(2)	0.6	0.6	0.6	0.7	0.9	0.4
Fines(3)	3.4	5.3	4.2	4.5	5.1	5.0
Sand	84.8	82.7	83.4	82.9	82.4	82.5

(1) Grams of oil recovered, wt %.
(2) 100 - (Grams of oil and solids recovered).
(3) Solids recovered in froth and water phase.

V1-Table 9

Effect of Air Rate on Oil Recovery and Froth Composition for a Poor Quality Tar Sand - Area D, Hole 11

Feed: A sample of Area D, Hole 11 contained 11.3% oil, 1.9% water and 86.8% solids

Air Rate, Cubic Feet Per Hour	**0.0**	**0.1**	**0.2**	**0.5**	**2.0**	**3.5**
Results, Wt %						
Froth Composition						
Water	65.8	54.6	50.0	53.3	48.1	47.9
Solids	5.6	9.4	12.3	11.4	18.5	21.0
Oil	28.6	36.0	37.7	35.3	33.4	31.1
Solids to Oil Ratio	0.20	0.26	0.33	0.32	0.55	0.67
% Wet Froth from 1st Aeration	77	50	53	47	72	68
Yields (Water Free Basis)						
Froth	3.2	10.1	11.7	12.4	16.8	17.7
Water Phase	11.8	6.4	4.8	4.9	3.4	3.0
Sand	84.9	83.5	83.5	82.7	79.8	79.3
Oil Recoveries in (Output)						
Froth	24.1	71.1	80.2	84.2	94.9	93.5
Water Phase	64.5	21.0	12.3	11.2	2.7	4.1
Sand	11.4	7.9	7.5	4.6	2.3	2.5
Tar Sand Composition (cal^c)						
Oil(1)	11.2	11.0	10.8	10.8	11.1	11.1
Water(2)	2.3	2.2	2.2	2.3	2.2	2.3
Fines(3)	4.8	6.0	6.2	6.5	8.9	9.5
Sand	81.7	80.8	80.8	80.4	77.8	77.2

(1) Grams of Oil recovered, wt %.
(2) 100 - (grams of Oil and Solids recovered).
(3) Solids recovered in froth and water phase.

V1-Table 10

Effect of Air Rate on Oil Recovery and Froth Composition for a Poor Quality Tar Sand - Area 4

Feed: A sample of Area 4 (9 months cold storage at ~40°F) contained 8.9% oil, 4.0% water and 87.1% solids

Air Rate, cupic feed per hour	**0.0**	**0.1**	**0.2**	**0.5**	**2.0**	**3.5**
Results, Wt %						
Froth Composition						
Water	74.4	45.3	47.8	47.2	50.9	49.8
Solids	8.0	24.3	26.4	28.3	28.0	28.9
Oil	17.6	30.4	25.8	24.5	21.1	21.3
Solids to Oil Ratio	0.46	0.80	1.03	1.15	1.33	1.36
% Wet Froth from 1st Aeration	87	52	58	64	71	66
Yields (Water free basis)						
Froth	1.0	9.4	13.6	15.9	19.1	20.5
Water Phase	15.2	10.7	19.5	6.6	5.7	4.9
Sand	83.8	79.9	66.9	77.5	75.2	74.6
Oil Recoveries In (Output)						
Froth	7.5	55.6	71.2	78.0	89.9	91.5
Water Phase	75.4	33.6	22.5	15.5	2.4	4.7
Sand	17.1	10.8	6.3	6.5	7.7	3.7
Tar Sand Composition (cal^{c})						
Oil(1)	9.1	9.0	9.1	9.0	9.4	9.1
Water(2)	5.0	3.8	3.9	4.5	5.6	4.1
Fines(3)	7.8	11.2	23.3	13.0	12.4	15.6
Sand	78.1	75.9	63.7(4)	73.5	72.5	71.2

(1) Grams of oil recovered, Wt %.
(2) 100 - (grams of oil and solids recovered).
(3) Solids recovered in froth and water phase.
(4) Sand decanted into water phase during separation.

V1-Table 11

Effect of Air Rate on Oil Recovery and Froth Composition for a Poor Quality Tar Sand - Area D, Hole 9

Feed: (A) Sample of Area D Hole 9 contained 10.1% oil, 3.2% water, and 86.7% solids
(B) Sample contained 9.7% oil, 4.2% water, 86.1% solids

Tar Sand Sample(1)	(A)				(B)					
Symbol in Figure	☐				o					
Air Rate, cubic feet per hour	**0.0**	**0.1**	**0.5**	**2.0**	**0.1**	**0.2**	**0.5**	**1.0**	**2.0**	**3.5**
No. of Aerations	2				3					
Results, Wt %										
Total Froth Composition										
Water	62.1	54.6	56.9	50.8	52.1	51.4	53.4	53.6	51.3	49.9
Solids	7.1	11.0	12.2	22.0	14.1	13.4	17.0	21.6	24.2	25.4
Oil	30.8	34.5	30.9	27.3	23.9	35.2	29.6	24.8	24.6	24.7
Solids/oil ratio	0.23	0.32	0.39	0.81	0.42	0.38	0.57	0.87	0.98	1.03
% Wet Froth from 1st Aeration	89	54	49	59	42	42	48	52	64	54
Yields (water free basis)										
Froth	3.4	10.3	10.9	17.1	10.5	11.7	13.2	16.2	18.9	18.3
Water Phase	9.6	5.6	4.8	3.8	5.7	4.7	4.7	3.7	3.4	3.3
Sand	87.0	84.2	84.3	79.1	83.8	83.6	82.1	80.1	77.7	78.4
Oil Recoveries in (output)										
Froth	28.9	74.3	79.3	89.8	78.9	85.9	86.8	93.0	95.2	95.6
Water Phase	58.1	17.7	13.0	5.0	16.1	8.6	9.2	3.2	2.7	2.2
Sand	13.0	8.0	7.7	5.2	5.0	5.5	4.0	3.8	2.1	2.2
Tar Sand Composition (cal^{c})										
Oil(2)	9.2	10.2	9.5	10.2	9.0	9.6	9.3	8.9	9.8	9.1
Water(3)	4.8	2.8	3.8	3.1	4.3	3.4	3.6	3.8	2.7	4.0
Fines(4)	4.4	6.0	6.4	10.5	6.9	6.8	8.3	10.5	12.1	11.9
Sand	81.6	81.0	80.3	76.1	79.8	80.2	78.8	76.8	75.4	75.0

(1) From the same large batch.
(2) Grams of oil recovered, wt %.
(3) 100 - (grams of oil and solids recovered).
(4) Solids recovered in froth and water phase.

V1-Table 12

Effect of Air Rate with Fresh Spot Samples of Area B, Area Holes 9, and 11, Tar Sands

Feeds: Area B, tar sand contained 12.8% oil, 11.5% water and 75.7% solids
Area D, Hole 9 contained 10.1% oil, 3.2% water and 86.7% solids
Area D, Hole 11 contained 8.6% oil, 4.0% water and 87.4% solids

Tar Sand Area (Hole No.)	**B**			**D(9)**			**D(11)**		
Air Rate, cubic feet per hour	**0.0**	**0.2**	**2.0**	**0.0**	**0.2**	**2.0**	**0.0**	**0.2**	**2.0**
Results, Wt %									
Total Froth Composition									
Water	22.5	26.1	39.6	38.7	44.9	41.5	62.1	55.6	50.0
Solids	6.7	9.0	12.9	4.6	4.9	7.9	13.0	17.0	25.1
Oil	70.8	64.9	47.5	56.7	50.2	50.6	24.9	27.4	24.9
Solids/Oil Ratio	0.10	0.14	0.27	0.08	0.10	0.16	0.52	0.62	1.01
% Wet Froth From 1st Aeration	92	96	91	82	81	88	96	55	75
Yields (Water Free Basis)									
Froth	15.4	16.6	18.4	8.3	11.0	12.1	1.9	8.9	13.5
Water Phase	2.1	1.8	2.0	4.7	3.3	2.3	13.9	9.2	7.8
Sand	82.5	81.6	79.6	87.0	85.7	85.6	84.2	81.9	78.7
Oil Recoveries in (output)									
Froth	98.7	99.2	99.8	74.4	95.6	96.8	14.4	64.1	77.6
Water Phase	1.3	0.6	0.2	22.0	2.6	2.2	67.3	24.2	11.5
Sand	0.0	0.2	0.0	3.6	1.8	1.0	18.3	11.7	10.9
Tar Sand Composition (cal^{c})									
Oil(3)	13.0	13.1	12.7	10.0	10.1	10.4	8.3	8.2	8.3
Water(4)	9.4	10.7	12.0	3.5	3.2	3.3	5.4	4.4	4.7
Fines(5)	2.9	3.6	5.2	2.9	5.5	3.6	8.1	10.1	13.0
Sand	74.7	72.6	70.1	83.6	81.2	82.7	78.2	77.3	74.0

(1) Wt % on total froth.
(2) Essentially the same as input; see analysis at top of table.
(3) Grams of oil recovered wt %.
(4) 100 - (Grams of oil and solids recovered).
(5) Solids recovered in froth and water phase.

V1-Table 13

Effect of Temperature with a "High Water" Area B Tar Sands

Tar Sand sample received was like a paste and contained 13.3 wt % water, 10.7 wt % oil, 6.3 wt % 325-Fines and 69.7% wt % sand. Migration of water to the top of the can occurred on standing (and presumably oil to the bottom) The sample was homogenized by stirring.

Experiment No. B	**1**	**2**	**3**	**4**	**5**	**6**
Temperature, °F	**140**	**150**	**160**	**170**	**180**	**190**
Results, Wt %						
Froth Composition						
Water	25.6	25.6	21.7	29.3	30.7	26.9
Solids	23.4	21.1	20.8	16.8	15.6	21.1
Oil	51.0	53.3	57.5	53.9	53.7	52.0
Solids/Oil Ratio	0.46	0.40	0.36	0.31	0.29	0.41
Wet Froth(1) From						
First Skimming	91	95	95	91	80	74
Second Skimming	9	5	5	9	20	26
Yields (Water Free Basis)						
Froth	17.9	17.0	17.5	15.8	15.2	17.2
Water Phase	5.5	5.5	5.3	5.3	6.1	5.8
Sand	76.6	77.5	77.2	78.9	78.7	77.0
Oil Recovery in (output)(2)						
Froth	98.1	97.1	96.3	96.4	96.9	90.4
Water Phase	1.7	1.9	1.6	1.5	2.1	3.2
Sand	0.2	1.0	2.1	2.1	1.0	6.4
Tar Sand Composition (cal^c)						
Oil(3)	10.8	10.6	11.6	10.8	10.6	11.6
Water(4)	13.8	15.2	13.3	13.8	13.1	14.6
Fines(5)	9.4	8.6	8.4	7.6	8.1	8.8
Sand	66.0	65.6	66.7	67.8	68.2	65.0

(1) Wt % on total froth.
(2) Essentially the same as input; see analysis at top of table.
(3) Grams of oil recovered wt %.
(4) 100 - (Grams of oil and solids recovered).
(5) Solids recovered in froth and water phase.

V1-Table 14

Effect of Temperature with a New Area 4 Tar Sands

Tar Sand feed contained 8.6 wt % oil, 4.7 wt % water, 86.7 wt % solids. A spot sample was homogenized and sieved.

Temperature, °F	**150**	**170**	**190**
Results, Wt %			
Froth Composition			
Water	44.9	49.3	50.3
Solids	32.6	25.3	22.2
Oil	22.5	25.4	27.5
Solids/Oil Ratio	1.45	1.00	0.81
Wet Froth(1) From			
First Skimming	68	63	61
Second Skimming	32	37	39
Yields (Water Free Basis)			
Froth	15.4	13.0	11.4
Water Phase	10.2	10.6	11.1
Sand	74.4	76.4	77.5
Oil Recovery in (output)			
Froth	76.0	75.4	75.1
Water Phase	15.3	19.9	21.9
Sand	8.7	4.7	3.0
Tar Sand Composition (cal^c)			
Oil(2)	8.2	8.1	7.8
Water(3)	5.3	5.9	7.1
Fines(4)	16.8	14.4	13.4
Sand	69.7	71.6	71.7

(1) Wt % on total froth.
(2) Grams of oil recovered wt %.
(3) 100 - (Grams of oil and solids recovered).
(4) Solids recovered in froth and water phase.

V1-Table 15

Area D Tar Sand Sample From Cut Adjacent to Hole 9 Contained Two Types of Tar Sands Separable by Dry Sieving

Tar Sand Sieved Samples Percent of Total	First Pass 59.7				Second Pass 40.3			
Operating Temperature, °F	-	150	180		-	150	180	
Results, Wt %								
Froth Composition								
Water	-	41.1	44.6	42.8	-	41.4	49.0	48.5
Solids	-	21.8	16.2	17.7	-	19.7	12.1	11.9
Oil	-	37.1	39.2	39.5	-	38.9	38.9	39.6
Solids/Oil Ratio	-	0.59	0.41	0.45	-	0.51	0.31	0.30
Wet Froth(1) From								
First Aeration	-	62.4	62.5	60.8	-	54.5	49.3	46.8
Second Aeration	-	37.6	37.5	39.2	-	45.5	50.7	53.2
Yields (Water Free Basis)								
Froth	-	17.6	16.8	17.1	-	13.7	12.0	12.2
Water Phase	-	3.4	2.7	2.7	-	4.5	5.4	4.9
Sand	-	79.0	80.5	80.2	-	81.8	82.6	82.9
Oil Recovery (output)(2)								
Froth	-	89.7	97.1	96.7	-	71.4	71.7	71.8
Water Phase	-	7.7	1.7	1.9	-	20.0	25.0	23.5
Sand	-	2.6	1.2	1.4	-	8.6	3.3	4.7
Tar Sand Composition, Cal^c								
Oil(3)	11.4	11.6	11.4	11.4	12.0	12.1	12.0	12.3
Water(4)	6.8	6.6	6.8	6.9	5.6	5.3	5.8	5.6
Fines(5)	81.8	8.4	6.9	7.2	82.4	6.2	4.8	4.4
Sand	81.8	73.4	74.9	74.5	82.4	76.4	77.4	77.7

(1) Wt % on total froth.
(2) Essentially the same as input; see analysis of feed.
(3) Grams of oil recovered, wt %.
(4) 100 - (Grams of oil and solids recovered).
(5) Solids recovered in froth and water phase.

V1-Table 16

Effect of Temperature with an Area D, Hole 11, Tar Sands

Temperature, °F	40	80	87	92	104	114	120	140	150	160	160	170	180	180	190	200
Operator	#1		#2				#1		#2		#1	#2		#1	#2	#1
Tar Sand Sample	#2		#2				#1		#2		#1	#2		#1	#2	#1
Homogenizing Method[1]	#2		#2				#1		#2		#1	#2		#1	#2	#1
Results, Wt %																
Froth Composition																
Water	55.0	45.3	42.4	42.5	41.0	42.2	38.8	42.3	42.0	43.8	44.8	45.9	45.2	47.3	45.8	42.2
Solids	26.0	26.9	31.4	32.5	31.5	26.3	22.0	16.2	21.3	21.4	15.9	16.9	19.9	14.7	17.7	17.9
Oil	19.0	27.8	26.2	25.0	27.5	31.5	39.2	41.5	36.7	34.8	39.3	37.2	34.9	38.0	36.5	39.9
Solids/Oil Ratio	1.37	0.97	1.20	1.30	1.15	0.83	0.56	0.39	0.58	0.61	0.41	0.45	0.39	0.39	0.48	0.45
Wet Froth[2] From																
First Skimming	50	63	63	68	83	80	84	79	74	70	78	68	75	82	75	83
Second Skimming	50	37	37	32	17	20	16	21	26	30	22	32	25	18	25	17
Yields (Water Free Basis)																
Froth	4.0	8.7	17.3	22.9	21.2	20.1	16.2	14.6	16.6	16.2	15.4	15.0	15.7	13.5	15.5	16.1
Water Phase	7.5	8.9	6.7	3.4	3.0	3.1	5.6	4.7	3.5	3.6	5.1	3.3	3.7	4.7	3.3	4.5
Sand	88.5	82.4	76.0	73.7	75.8	76.8	78.2	80.7	79.9	80.2	79.5	81.7	80.6	81.8	81.2	79.4
Oil Recovery in (output)																
Froth	16.3	41.4	73.6	87.5	89.7	94.6	92.9	96.3	96.4	94.8	96.6	95.6	95.0	94.3	97.0	95.9
Water Phase	38.8	33.4	15.0	4.5	3.3	2.7	3.8	2.0	2.9	3.4	2.3	2.7	3.5	4.0	2.2	3.3
Sand	44.9	25.2	11.4	8.0	7.0	2.7	3.3	1.7	0.7	1.8	1.1	1.7	1.5	1.7	0.8	0.8
Tar Sand Composition																
Oil[3]	9.8	10.0	10.3	11.0	10.6	11.3	10.7	10.4	10.5	10.2	10.8	10.3	10.1	9.8	10.4	11.2
Water[4]	6.0	6.6	4.0	3.3	3.6	2.8	4.1	4.6	3.6	3.9	4.1	4.0	4.2	5.1	3.9	3.8
Sand	78.5	74.5	71.8	70.4	72.2	74.3	74.6	76.9	76.9	76.8	76.2	78.3	77.0	77.4	77.8	76.3
Fines	5.7	8.9	13.9	15.3	13.6	11.6	10.6	8.1	9.0	9.1	8.9	7.4	8.7	7.7	7.9	8.7
Sand	78.5	74.5	71.8	70.4	72.2	74.3	74.6	76.9	76.9	76.8	76.2	78.3	77.0	77.4	77.8	76.3

(1) See page 1.
(2) Wt % on total froth.
(3) Grams of oil recovered wt %.
(4) 100 - (Grams of oil and solids recovered).
(5) Solids recovered in froth and water phase.

V1-Table 17

Effect of Tar Sand "pH" on Processability

Average oil recoveries and froth composition are from laboratory extractions using procedure for the standard Brass Pot separation and pH measurements were made on the water phase from extractions at equivalent amounts of water in separation.

Tar Sand			Hot Water Flotation								
Area(1) (Hole No.)	Oil, Wt % Dry Basis	Wt % 325-(2) on Solids	pH Range(3) on Sep^{d} Water Phase	No. of Tests	Average pH	Oil Recovery, Wt % -- 1st Aeration (4)	Oil Recovery, Wt % -- 2nd Aeration	Froth Composition Water	Froth Composition Solids	Froth Composition Oil	Solids in Water Phase and Froth
B	14.4	3.2	8.8 - 9.0	3	8.9	91	99.8	40	13	47	5.2
B	14.9	8.2	8.3 - 8.7	5	8.4	78	97	31	16	54	8.1
B	12.4	8.0	8.0 - 8.5	13	8.3	87	96	27	20	54	8.4
D (10)	12.4	-	7.6 - 8.2	6	7.9	61	97	40	13	47	5.0
B	11.2	5.0	7.7 - 7.9	6	7.8	85	96	32	17	51	5.1
D (11)	11.0	-	7.4 - 7.7	7	7.6	73	94	45	17	38	8.0
D (9)	10.3	1.6	7.4 - 7.6	3	7.5	85	97	42	8	51	3.6
D (9)	9.9	10.8	7.4 - 7.7	3	7.5	72	93	45	22	33	10.4
D (4)	9.3	10.1	7.1 - 7.7	6	7.4	62	90	49	31	20	12.4
D (9)	9.9	8.0	6.7 - 7.0	7	6.8	54	83	51	20	29	8.6
D (9)	10.1	10.6	6.7 - 7.0	10	6.8	52	88	50	22	28	12.1
D (11)	11.5	-	6.5 - 6.6	5	6.6	58	92	48	19	33	9.0
D (10)	10.5	6.1	6.3 - 6.9	6	6.6	55	80	54	12	34	6.2
D (11)	9.0	-	6.0 - 6.8	4	6.4	58	78	50	25	25	13.0
D (10)	12.2	2.1	6.0 - 6.7	4	6.4	43	79	46	6	48	3.3
21A(5)	6.9	18.1	6.3 - 6.4	3	6.3	50	75	55	31	14	28.6

(1) Fresh samples (as received) and samples stored cold (~40°F)
(2) Obtained by wet screening of solids from soxhlet extraction of tar sands
(3) On different samples from the same homogenized tar sand
(4) Very approximate and low based on ratio of wet froth from aerations
(5) At standard conditions, but with 0.2 cubic feet/hour of air

V2

INORGANIC ADDITIVES IN SLURRYING

V2-Table 1

Effect of Sodium Salt Concentration on Processability of a Poor Quality Tar Sand (Hole 21A Tar Sand Containing 5.4 % Oil, 7.2 % Water, 31.5 % 200-Fines, 55.9 % Sand)

Sodium Salt	None	Hydroxide			Sulphide			Carbonate		
Sodium in Mixing Sol^n Wt % on Tar Sand	0.0	0.045	0.09	0.18	0.045	0.09	0.18	0.045	0.09	0.18
lbs Sodium Salt (Anhydrous) per ton of Tar Sands	0.0	1.57	3.14	6.28	1.53	3.06	6.12	2.08	4.16	8.32
Froth Composition, Wt %(1)										
Water	53.7	49.2	40.7	35.6	50.0	50.3	45.0	54.1	45.9	45.2
Solids	32.8	29.0	27.1	46.3	39.0	34.9	28.8	25.7	24.7	25.2
Oil	13.5	21.8	32.2	18.1	11.0	14.8	26.2	20.2	29.4	29.6
Solids/Oil Ratio	2.43	1.33	0.84	2.56	3.55	2.36	1.10	1.27	0.84	0.85
Oil Recovery In Froth Wt %(2)	46.5	63.3	43.2	17.5	30.4	28.2	24.4	58.5	60.5	53.1
pH of Separated Water Phase	5.5	8.7	9.0	9.4	8.0	9.0	11.0	8.1	8.1	8.9

Sodium Salt	Silicate			Tripolyphosphate			Na_2S(3)	Na_2CO_3(3)	Na_2SO_3(3)	$Na_5P_8O_{10}$(3)
Sodium in Mixing Sol^n Wt % on Tar Sand	0.045	0.09	0.18	0.045	0.09	0.18	0.09			
lbs Sodium Salt (Anhydrous) per ton of Tar Sands	2.34	4.79	9.58	2.90	5.80	11.60	3.10	3.65	3.91	4.47
Froth Composition, Wt %(1)										
Water	43.2	38.7	33.7	45.3	42.2	29.0	48.0	41.0	35.8	37.6
Solids	29.5	34.2	16.2	28.5	26.8	21.7	35.2	27.2	26.6	26.3
Oil	27.3	27.1	50.1	26.2	31.0	49.3	16.8	31.8	37.6	36.1
Solids/Oil Ratio	1.08	1.26	0.32	1.09	0.86	0.44	2.10	0.86	0.71	0.73
Oil Recovery In Froth Wt %(2)	77.1	74.7	50.1	81.4	74.2	76.8	35.4	56.2	84.5	76.6
pH of Separated Water Phase	8.0	8.5	9.0	6.8	7.2	7.3	9.0	9.0	8.9	8.7

(1) Composite from two aerations.

(2) Input as ashes vs solid size were not available.

(3) 50/50 solution of salt and hydroxide of equivalent wt % Na.

V2-Table 2

Effect of Phosphate Type and Concentration on Separation of an Aged(1) Tar Sands Dug from a Surface Hole(2)

Conditions														
Additive: Sodium -	- Pyrophosphate -			Tripolyphosphate								Hexametaphosphate		
Formula	$Na_4P_2O_7$			$Na_5P_3O_{10}$								$(NaPO_3)_6$		
Sodium Added, wt % on Tar Sand	0.21	0.42	0.84	0.21	0.31	0.42	0.52	0.84	0.94	1.05	1.25	0.21	0.42	0.84
lb Salt/Ton of T.S.	18.1	36.2	72.5	12.0	18.0	24.0	30.0	48.0	54.0	60.0	72.0	16.5	33.0	66.0
pH of Solution	10.2	10.1	9.9	9.5	9.5	9.4	9.3	9.1	9.1	9.1	9.0	6.6	6.4	6.1
Results, wt %														
Froth Composition														
Water	38.1	28.5	33.8	43.4	31.3	29.8	29.8	29.4	27.1	28.1	32.9	37.5	35.4	32.9
Solids	34.7	33.8	22.2	32.0	34.1	29.3	30.0	23.6	23.1	21.6	22.9	39.2	36.4	28.3
Oil	27.3	37.7	44.0	24.5	34.6	41.0	40.3	47.1	49.9	50.3	44.1	23.4	28.3	38.8
Solids/Oil Ratio	1.27	0.90	0.51	1.30	0.98	0.72	0.75	0.50	0.46	0.43	0.52	1.67	1.29	0.73
Yields (Dry Basis)														
Froth	9.1	11.6	11.2	10.1	14.4	13.0	15.8	12.3	11.6	11.6	12.5	11.3	10.6	12.1
Water Phase	8.6	10.0	11.2	9.5	7.2	7.8	9.8	11.3	10.8	11.5	12.0	8.2	11.0	11.1
Sand	82.2	78.4	77.5	80.3	78.4	79.2	74.4	76.4	77.6	77.0	75.5	80.5	78.4	76.7
Oil Recovery														
Froth	47.2	77.4	81.1	51.1	80.3	82.1	87.6	86.8	83.6	83.9	87.9	48.3	51.9	75.4
Water Phase	20.7	17.3	17.1	23.5	9.8	12.3	11.0	12.2	14.0	14.4	11.3	19.4	25.7	16.6
Sand	32.0	5.3	1.8	25.4	9.9	5.6	1.4	1.0	2.4	1.8	0.8	32.3	22.3	8.0
Tar Sand Composition														
Oil	7.6	7.3	8.6	7.7	8.3	8.5	8.0	8.8	8.9	9.1	8.9	7.9	8.2	8.8
Water	10.7	8.1	7.0	10.2	8.6	8.0	6.0	6.8	6.3	5.7	5.3	10.1	8.1	5.1
Fines	10.7	12.9	12.5	11.9	12.3	11.1	12.0	13.3	12.3	12.8	14.4	12.2	13.5	13.9
Sand	71.0	71.7	72.0	70.2	0.8	72.4	74.0	71.2	72.5	72.4	71.5	69.8	70.3	71.9
pH of Water Phase	4.4	6.7	8.6	4.1	6.1	6.7	6.8	7.8	7.9	8.1	8.3	3.1	3.6	5.1
Zeta Potential, mv	17.5	27.4	32.4	20.9	31.4	30.8	30.4	32.5	27.2	26.2	31.5	13.7	23.8	30.4

(1) 2 1/2 years storage in plastic bag at ambient temperatures.

(2) C.S.A. surface hole No. 10.

V2-Table 3

Effect of Phosphate Type and Concentration on Separation of an Aged(1) Tar Sands Dug from a Surface Hole(2)

Conditions													
Additive: Sodium Phosphate	Dequest(4)	Dequest(4)	Dequest(4)						-(3)	TPP(3)	-	-	-
Type	2000	2000	2006						-	-	-	-	-
lb/Ton of T.S.	70.4	17.4	68.8					17.2	-	48.0	-	-	-
Sodium Hydroxide, lb/Ton of T.S.	-	Note 5	-	0.81	1.63	2.43	3.25	Note 6	-	-	6.5	13.0	26.0
pH of Solution	0.7	9.6	7.5	11.8	12.2	12.5	12.5	11.0	5.8	9.2	12.5+		
Results, wt %													
Froth Composition													
Water	43.2	44.2	37.3	31.4	31.8	30.0	31.3	40.7	28.9	32.2	45.0	51.3	49.4
Solids	41.1	37.7	34.7	30.9	30.2	25.2	23.3	41.2	51.9	21.0	33.1	29.0	31.1
Oil	15.8	18.1	28.0	37.6	38.0	44.8	45.3	18.8	19.2	46.8	21.9	19.7	19.5
Solids/Oil Ratio	2.60	2.09	1.24	0.82	0.80	0.56	0.52	2.19	2.69	0.45	1.51	1.47	1.59
Yields (Dry Basis)													
Froth	12.2	7.8	11.7	11.9	11.0	10.4	9.2	11.8	16.6	11.2	9.2	10.4	8.7
Water Phase	9.1	11.3	8.3	10.3	10.4	10.0	12.0	9.5	5.8	11.0	12.6	15.5	14.8
Sand	78.7	80.9	80.0	77.8	78.6	79.7	78.8	78.7	77.6	77.9	78.2	76.1	76.5
Oil Recovery													
Froth	37.2	30.2	51.2	73.7	71.0	74.6	70.7	41.3	50.8	85.8	42.9	51.3	39.3
Water Phase	22.1	40.6	25.9	16.9	21.2	16.8	22.5	25.1	14.5	12.1	31.2	33.9	36.6
Sand	40.7	29.2	22.8	9.4	7.8	8.6	6.8	33.7	34.8	2.1	25.9	14.8	24.1
Tar Sand Composition													
Oil	8.2	7.3	9.2	8.2	7.9	8.2	7.9	7.9	8.0	8.4	7.7	7.3	8.0
Water	10.1	12.1	9.5	7.8	8.2	7.8	8.1	11.5	9.7	6.5	10.7	11.2	6.0
Fines	14.3	11.6	10.9	13.0	12.3	11.2	12.1	13.6	15.0	12.5	13.8	15.0	16.0
Sand	67.4	69.0	70.3	71.0	71.6	72.8	71.9	67.0	67.3	72.7	67.8	66.5	70.0
pH of Water Phase	1.6	3.6	5.8	7.1	7.9	9.1	9.7	3.2	3.3	7.6	6.8	11.1	12.2
Zeta Potential, mv	14.0	9.8	28.5	26.2	27.2	24.8	28.7	9.5	17.5	38.4	17.6	25.2	12.5

(1) 2 1/2 years storage in plastic bag at ambient temperatures.
(2) C.S.A.surface hole No. 10.
(3) Left soaking after mixing for 1 hr at 180°F prior to flooding.
(4) Monsanto product.
(5) Sodium hydroxide added to change pH from 0.7 to 9.6.
(6) Sodium hydroxide added changed pH from 7.9 to 11.0.

V2-Table 4

Effect of Sodium Salts and pH on Various Tar Sands

Tar Sand Sample	Bitumount						Hole 21A**				15-16-2 Top**			
	1 and 2*	1	2	2	1	2								
Solution in Mixing	DW	Na_2SiO_3	NaTPP	Na_2SiO_3	NaOH	NaOH	-	NaTPP	Na_2SiO_3	NaOH	-	NaTPP	Na_2SiO_3	NaOH
Sodium in Mixing Sol^{n} Wt % on Tar Sand	-	0.068	0.090	0.090	0.045	0.090	-	0.090			-	0.090		
lb Sodium Salt (Anhydrous) per Ton of Tar Sands	-	3.59	5.80	4.79	1.57	3.14	-	5.80	4.79	3.14	-	5.80	4.79	3.14
Results, Wt %														
Froth Composition														
Water		31.5	20.4	21.9	27.7	22.0	57.0	38.2	44.8	50.3	58.3	59.6	58.2	58.7
Solids		33.0	22.3	22.8	33.8	31.8	23.2	24.9	23.8	20.2	23.7	25.1	26.5	26.3
Oil		55.5	57.3	55.3	38.6	46.2	19.8	36.9	31.5	29.5	17.9	15.3	15.4	15.1
Solids/Oil Ratio		0.93	0.39	0.41	0.88	0.69	1.17	0.67	0.76	0.69	1.32	1.63	1.72	1.74
Yields (Dry Basis)														
Froth		18.9	19.6	20.2	25.2	24.1	17.3	14.0	14.0	8.7	6.8	8.7	9.5	2.6
Water Phase		7.0	2.7	2.5	3.1	2.4	9.7	12.9	11.5	16.4	16.8	14.5	15.3	30.7
Sand		74.1	77.7	77.2	71.7	73.5	73.0	73.2	74.5	74.9	76.4	76.8	75.2	67.??
Oil Recovery														
Froth		71.1	89.1	95.7	92.1	90.8	82.0	87.6	85.0	53.9	48.9	67.6	65.0	16.??
Water Phase		23.1	10.2	3.9	7.7	4.3	11.1	12.1	13.4	43.1	39.0	32.0	27.1	83.3
Sand		5.8	0.6	0.4	0.2	4.8	6.9	0.3	1.7	3.0	12.1	0.5	7.9	0.0
Tar Sand Comp^{n} (Cal^{c})														
Oil		13.5	15.8	14.9	14.5	15.8	8.6	8.4	8.4	8.6	5.5	4.6	4.9	4.7
Water		1.5	0.3	0.5	0.7	0.2	11.2	11.5	10.8	10.4	8.5	9.0	8.5	8.3
Fines		12.7	6.6	7.8	13.7	11.6	16.0	15.3	14.5	14.2	16.8	16.8	18.2	25.3
Sand		72.2	77.3	76.8	71.1	72.6	64.2	64.7	66.3	66.9	69.2	69.6	68.4	61.7
pH of Water Phase	3.1	8.0	8.3	9.5	11.7	12.2	7.4	8.4	9.9	12.2	6.8	7.8	8.9	12.2

* Sample #1 was a small amount (lb) of tar sands from National Research Council (Ottawa)
Sample #2 was a second tar sands presumably from the same batch received a year later.
** Characterization samples.

No Separation

V2-Table 5

Chemical Adjusted Processability of Beaver River Tar Sands

Tar Sand (Designation)	Plant Feed						
Tri Poly-							
Sodium Additive (In Mixing)	**None**	**Phosphate**	**Carbonate**	**Hydroxide**			**Silicate**
Amount of Salt Wt % on T.S.	0	0.80	0.57	0.12	0.28	0.40	0.66
Amount of Sodium Wt % on T.S.	0	0.24	0.24	0.07	0.16	0.23	0.24
No Aeration Froth							
Sands/Oil Ratio	0.32	0.15	0.17	0.16	0.22	0.20	0.10
Water/Oil Ratio	0.89	0.83	0.72	0.44	0.99	0.87	0.50
Oil Recovery, Wt %	89.1	89.0	87.0	87.9	87.3	86.0	85.5
No + 1st Aeration Froths							
Solids/Oil Ratio	0.38	0.20	0.21	0.19	0.24	0.21	0.12
Water/Oil Ratio	1.08	0.90	0.80	0.46	1.00	0.87	0.53
Oil Recovery, Wt %	92.5	90.3	88.5	90.7	89.3	88.6	88.5
No + 1st and 2nd Aeration Froths							
Solids/Oil Ratio	0.50	0.29	0.35	0.27	0.27	0.26	0.19
Water/Oil Ratio	1.51	0.90	0.93	0.50	1.00	0.90	0.68
Oil Recovery, Wt %	95.1	94.6	92.0	95.2	93.9	93.6	89.2
Oil Loss In Water Phase	3.7	5.4	8.0	4.6	6.1	6.3	10.5
Oil Loss In Sand Phase	1.2	0.0	0.0	0.2	0.0	0.1	0.2
Water Phase: pH$_2$	8.2	8.8	10.3	9.9	10.9	11.2	11.8
Zeta Potential ZP$_1$	26	52	62	44	56	41	55
ZP$_2^{(1)}$	34	54	(80)	43	(73)	(53)	(72)
Conductance, C$_2$	816	5576	7820	1122	4760	6120	8500

(1) Values in parenthesis are estimated from

V2-Table 6

Chemical Adjusted Processability of Beaver River Tar Sands

Tar Sand (Designation)	--- Good ---		------------- Intermediate -------------				
Sodium Additive (In Mixing)	None	Hydroxide	None	Tripoly-Phosphate	Hydroxide	Carbonate	Silicate
Amount of Salt, Wt % On T.S.	0	0.12	0	0.80	0.12	0.57	0.66
Amount of Sodium, Wt % On T.S.	0	0.07	0	0.24	0.07	0.24	0.24
No Aeration Froth							
Solids/Oil Ratio	0.19	0.20	0.35	0.21	0.25	0.20	0.10
Water/Oil Ratio	0.64	0.68	0.76	0.79	0.72	0.54	0.43
Oil Recovery, Wt %	75.9	84.0	86.8	83.9	85.9	59.4	80.7
No + 1st Aeration Froths							
Solids/Oil Ratio	0.25	0.21	0.40	0.23	0.28	0.22	0.16
Water/Oil Ratio	0.70	0.65	0.91	0.81	0.70	0.61	0.48
Oil Recovery, Wt %	91.5	89.7	93.5	85.9	90.4	81.3	84.1
No + 1st and 2nd Aeration Froths							
Solids/Oil Ratio	0.34	0.25	0.47	0.32	0.28	0.28	0.24
Water/Oil Ratio	1.01	0.64	1.19	0.84	0.71	0.72	0.54
Oil Recovery, Wt %	93.8	92.8	95.8	88.5	90.4	83.9	85.5
Oil Loss In Water Phase	4.8	6.8	3.5	11.0	8.8	13.7	14.5
Oil Loss In Sand Phase	1.4	0.4	0.7	0.5	0.8	2.4	0.0
Water Phase: pH_2	7.9	10.0	8.5	9.1	10.2	10.3	12.2
Zeta Potential ZP_1	35	47	34	55	43	49	53
ZP_2	52	(61)	59	49	66	(64)	(69)
Conductance C_2	1054	2210	952	5950	2040	8160	8908

V2-Table 7

Chemical Adjusted Processability of Beaver River Tar Sands

Tar Sand (Designation)	Bench No. 1							
Sodium Additive (in mixing)	**None**	**Tripoly Phosphate**	**Hydroxide**				**Carbonate**	**Silicate**
Amount of Salt, wt% Onts	0	0.80	0.08	0.12	0.16	0.24	0.57	0.66
Amount of Sodium, wt% Onts	0	0.24	0.05	0.12	0.09	0.14	0.24	0.24
No Aeration Froth								
Solids/Oil Ratio	0.29	0.22	0.42	0.25	0.18	0.18	0.15	0.08
Water/Oil Ratio	0.91	0.51	0.38	0.52	0.37	0.48	0.57	0.54
Oil Recovery, wt%	33.6	92.3	91.5	89.1	84.4	91.5	58.7	91.1
No + 1st Aeration Froths								
Solids/Oil Ratio	0.35	0.22	0.45	0.27	0.20	0.20	0.16	0.13
Water/Oil Ratio	1.08	0.55	0.49	0.58	0.41	0.50	0.65	0.58
Oil Recovery, wt%	86.7	93.0	94.9	95.3	93.3	94.0	71.3	92.9
No + 1st and 2nd Aeration Froths								
Solids/Oil Ratio	0.44	0.23	0.49	0.29	0.23	0.24	0.19	0.22
Water/Oil Ratio	1.37	0.59	0.68	0.63	0.42	0.51	0.63	0.64
Oil Recovery, wt%	93.0	96.3	96.2	97.7	95.5	95.5	90.4	92.9
Oil Loss in Water Phase	2.2	3.5	1.2	1.9	3.8	4.1	9.6	6.6
Oil Loss in Sand	4.8	0.2	2.6	0.4	0.7	0.4	0.0	0.5
Water Phase: pH_2	3.7	7.8	8.0	8.5	10.2	11.5	10.1	12.2
Zeta Potential, ZP	19	49	32	42	38	39	43	72
ZP_2	22	59	(42)	56	62	(50)	(56)	(94)
Conductance, C_2	1224	6528	-	2210	2584	4046	6800	11,560

V2-Table 8

Chemical Adjusted Processability of Beaver River Tar Sands

Tar Sand: Unit Feeds - Run No. (Designation)	------ 6 ----------					---------- 7 ----------				
Sodium Additive (In Mixing)	**None**	**Tripoly-Phosphate**	**Hydroxide**	**Carbonate**	**Silicate**	**None**	**Tripoly-Phosphate**	**Hydroxide**	**Carbonate**	**Silicate**
Amount of Salt, Wt % on T.S.	0	0.80	0.12	0.57	0.66	0	0.80	0.12	0.57	0.66
Amount of Sodium, Wt % on T.S.	0	0.24	0.07	0.24	0.24	0	0.24	0.07	0.24	0.24
No Aeration Froth										
Solids/Oil Ratio	0.24	0.10	0.22	0.18	0.11	0.29	0.16	0.25	0.18	0.10
Water/Oil Ratio	0.99	0.66	0.48	0.55	0.57	0.81	0.82	0.50	0.59	0.46
Oil Recovery, Wt %	39.0	91.2	89.3	78.3	84.6	88.2	91.4	91.1	92.0	88.6
No + First Aeration Froths										
Solids/Oil Ratio	0.35	0.13	0.24	0.22	0.15	0.40	0.24	0.30	0.21	0.13
Water/Oil Ratio	1.09	0.66	0.55	0.60	0.62	1.07	0.88	0.49	0.69	0.54
Oil Recovery, Wt %	89.5	94.0	93.5	88.5	85.4	92.3	91.9	94.2	92.2	88.6
No + 1st and 2nd Aeration Froths										
Solids/Oil Ratio	0.41	0.22	0.27	0.24	0.18	0.57	0.35	0.40	0.34	0.22
Water/Oil Ratio	1.22	0.70	0.56	0.67	0.70	2.21	0.89	0.59	0.77	0.56
Oil Recovery, Wt %	93.5	95.1	96.3	91.6	87.0	93.8	91.9	95.0	92.2	88.6
Oil Loss in Water Phase	4.2	4.9	3.6	8.1	12.1	4.3	7.6	4.5	7.1	11.5
Oil Loss in Sand Phase	2.3	0.0	0.1	0.3	0.8	1.9	0.5	0.5	0.6	0.1
Water Phase: pH_2	7.4	9.0	10.2	10.5	12.2	8.3	9.0	9.9	10.3	11.7
Zeta Potential ZP_1	19	52	36	40	57	23	57	38	65	61
ZP_2	20	55	56	(52)	(73)	36	46	44	(85)	(79)
Conductance, C_2	432	5,474	2,140	7,480	11,560	517	5,304	1,768	7,480	8,500

V2-Table 9

Chemical Adjusted Processability of Beaver River Tar Sands

Tar Sands (Designation)	------------------ Unit Feed - Run No. 9 --------------------							
Sodium Additivie in Mixing	**None**	**Tripoly Phosphate**	**-------- Hydroxide --------**				**Carbonate**	**Silicate**
Amount of Salt, wt% Onts	0	0.80	0.06	0.12	0.24	0.40	0.57	0.66
Amount of Sodium, wt% Onts	0	0.24	0.04	0.07	0.14	0.23	0.24	0.24
No Aeration Froth								
Solids/Oil Ratio	0.19	0.18	0.21	0.22	0.20	0.24	0.20	0.10
Water/Oil Ratio	0.58	0.82	0.39	0.37	0.71	0.92	0.64	0.50
Oil Recovery, wt%	86.5	89.7	87.0	87.0	82.2	90.5	87.1	84.3
No + 1st Aeration Froths								
Solids/Oil Ratio	0.25	0.19	0.24	0.29	0.23	0.25	0.23	0.13
Water/Oil Ratio	0.77	0.88	0.47	0.42	0.70	0.95	0.70	0.58
Oil Recovery, wt%	90.8	90.8	95.4	94.5	87.1	91.1	89.6	86.9
No + 1st and 2nd Aeration Froths								
Solids/Oil Ratio	0.34	0.42	0.36	0.36	0.28	0.29	0.31	0.22
Water/Oil Ratio	0.91	1.04	0.62	0.46	0.74	0.95	0.86	0.66
Oil Recovery, wt%	96.5	91.2	96.8	96.0	92.2	92.7	90.5	89.4
Oil Loss in Water Phase	2.0	7.6	2.6	3.8	5.1	6.6	6.9	9.3
Oil Loss in Sand Phase	1.5	1.6	0.6	0.2	2.7	0.6	2.6	1.3
Water Phase: pH_2	8.1	9.0	9.3	10.0	10.5	11.6	10.3	12.1
Zeta Potential ZP_1	18	53	30	39	37	50	51	69
ZP_2	26	49	41	47	58	58	(66)	(90)
Conductance C_1	296	5,712	918	1,632	2,992	6,460	7,140	10,880

V3

ORGANIC ADDITIVES IN SLURRYING

V3-Table 1

pH (Sodium Hydroxide) and Anion (Oxalate) Effects in Separation (Hole 11 Tar Sand and Nitrogen in Aeration)

Conditions														
Additive, 2lbs/Ton of T.S.	-	-	-	-	-	-	-	Oxalic Acid						
NaOH in Mixing Sol^n lbs/Ton of Tar Sand	-	0.81	1.63	2.44	2.85	3.25	4.06	-	0.81	1.63	2.44	2.85	3.25	4.06
Results, wt %														
Froth Composition														
Water	52.1	57.3	54.5	59.5	60.2	56.4	58.2	46.0	49.3	49.4	49.0	49.4	55.0	56.1
Solids	35.8	30.1	31.3	28.3	27.2	29.8	26.1	39.7	33.0	33.7	27.4	27.3	26.0	23.1
Oil	12.1	12.5	14.2	12.2	12.6	13.8	15.7	14.3	17.8	16.9	23.6	23.3	18.8	20.8
Solids/Oil Ratio	2.9	2.4	2.2	2.3	2.1	2.2	1.7	2.8	1.9	2.0	1.2	1.2	1.4	1.1
Yields (Dry Basis)														
Froth	13.4	10.6	9.6	10.3	12.6	13.6	10.6	13.7	11.3	11.6	7.0	10.7	11.0	9.4
Water Phase	4.2	6.2	5.5	8.1	7.6	9.5	8.5	4.1	5.7	6.4	10.1	11.6	8.3	10.4
Sand	82.4	83.1	84.9	81.6	79.7	76.9	80.9	82.2	83.0	81.9	82.8	77.7	80.6	80.3
Oil Recovery														
Froth	44.1	41.8	40.3	43.3	50.8	57.6	55.1	44.9	47.5	48.6	59.1	65.0	59.0	61.9
Water Phase	10.1	21.7	17.9	30.2	26.0	30.8	25.6	8.5	15.9	19.9	38.1	29.6	24.6	27.7
Sand	45.8	36.5	41.8	26.5	23.2	11.7	19.3	46.6	36.7	31.5	2.9	5.4	16.4	10.4
Tar Sand Composition														
Oil	6.9	6.6	6.8	6.4	7.2	6.7	6.6	7.3	7.5	7.2	6.5	6.8	7.1	6.5
Water	10.0	10.9	9.4	10.4	9.5	10.3	10.0	10.1	9.4	9.4	10.0	9.9	9.4	9.5
Fines	12.2	10.8	9.8	11.8	12.8	14.8	12.0	12.1	10.7	11.4	13.9	13.7	11.6	12.1
Sands	71.0	71.6	74.0	71.4	70.5	68.2	71.4	70.5	72.4	71.9	69.6	69.6	71.9	72.0
pH of Water Phase	3.7	3.6	5.6	8.1	8.5	9.8	10.9	2.8	3.6	4.3	8.0	8.5	8.9	9.9

V3-Table 2

Effect of Oxalate on Separation (Hole 11 Tar Sand and Nitrogen in Aeration)

Conditions									
Sodium Hydroxide, lbs/Ton of Tar Sand	3.25					4.87		6.50	
Additive	Oxalic Acid					Oxalic Acid			
Conc % on Tar Sand	-	0.1	0.2	0.3	0.4	0.5			
lbs/Ton of Tar Sand	-	2	4	6	8	10			
							(1)		(1)
Results, wt %									
Froth Composition									
Water	56.4	55.0	47.8	49.3	47.6	44.7	46.4	48.7	48.0
Solids	29.8	26.1	32.5	29.6	30.4	25.3	25.1	26.2	25.5
Oil	13.8	18.8	19.8	21.1	22.0	30.1	28.5	25.0	26.5
Solids/Oil Ratio	2.20	1.40	1.64	1.40	1.38	0.84	0.88	1.05	0.96
Yields (Dry Basis)									
Froth	13.6	11.0	16.3	13.8	13.4	9.1	8.1	8.2	7.2
Water Phase	9.5	8.3	6.7	6.8	7.7	12.5	12.3	13.4	13.4
Sand	76.9	80.6	77.1	79.4	78.9	78.4	79.6	78.4	79.5
Oil Recovery									
Froth	57.6	59.0	71.1	68.2	73.2	64.2	56.3	55.9	49.1
Water Phase	30.8	24.6	12.6	15.8	16.7	31.3	38.4	36.2	43.4
Sand	11.7	16.4	16.3	16.0	10.2	4.5	5.2	8.0	7.4
Tar Sand Composition									
Oil	6.7	7.1	7.9	7.6	7.2	7.1	7.0	6.6	6.8
Water	10.3	9.4	9.2	9.6	6.8	7.8	8.7	8.3	8.4
Fines	14.8	11.6	14.3	12.2	13.2	13.1	12.0	13.7	12.5
Sand	68.2	71.9	68.7	70.6	72.8	71.9	72.3	71.4	72.3
pH of Water Phase	9.8	8.9	7.1	6.7	6.3	11.8	11.8	11.9	11.9
Zeta Potential, MV	-	-	-	-	-	25.1	24.7	21.5	28.4

(1) Left standing at 180°F for one hour after mixing and prior to flooding.

V3-Table 3

Effect of Pyridine and Stannous Chloride on Separation (Hole 11 Tar Sands and Nitrogen in Areration)

Conditions									
Additive (wt % on tar sand)	-$^{(1)}$Pyridine(0.1)$^{(1)}$ -			- - - - Sn Cl_2(0.6)$^{(2)}$- - - - - -				Hydroxylamine (0.1)	
Sodium Hydroxide									
lbs/Ton of Tar Sand	-	-	-	0.81	1.63	2.85	3.25	- - - - 2.85 - - - -	
Results, wt %									
Froth Composition									
Water	45.0	54.0	54.5	40.5	49.3	48.6	52.2	60.2	48.0
Solids	19.1	15.0	34.8	50.7	40.4	25.6	21.1	27.2	31.2
Oil	35.9	31.0	10.7	8.7	10.3	25.8	26.7	12.6	20.8
Solids/Oil Ratio	0.53	0.48	3.20	5.79	3.92	0.99	0.79	2.1	1.50
Yields (Dry Basis)									
Froth	13.5	12.7	8.6	21.9	10.1	7.6	6.1	12.6	13.3
Water Phase	3.9	4.1	3.5	3.1	8.2	11.5	10.8	7.6	10.7
Sand	82.6	83.2	87.9	75.0	81.7	80.8	83.1	79.7	76.0
Oil Recovery									
Froth	81.7	83.9	29.8	37.2	27.7	49.4	43.8	50.8	68.5
Water Phase	9.8	12.9	8.4	6.2	29.7	36.8	40.3	26.0	27.7
Sand	8.5	3.2	61.9	56.6	42.6	13.8	15.8	23.2	3.9
Tar Sand Composition									
Oil	10.4	9.9	7.3	8.0	6.9	7.3	7.3	7.2	7.0
Water	3.2	3.3	10.0	7.5	6.9	6.2	6.4	9.5	9.6
Fines	7.3	6.7	8.4	19.6	13.1	11.7	9.7	12.8	14.9
Sand	79.1	80.2	74.2	64.9	73.1	74.8	76.6	70.5	68.5
pH of Water Phase	6.3	7.2	2.8	4.0	6.0	9.9	11.7	8.5	10.6

(1) Different sample of Hole 11 used in these experiments.

(2) Cold pretreatment with 2% solution prior to sodium hydroxide addition and hot water separation.

V3-Table 4

Exploratory Experiments with Additives and Different Tar Sands (Nitrogen in Aeration)

Tar Sand	Hole 11									Hole 21A		
Additive: 2 lbs per	-	SnCl$_2$	SnCl$_2$	Zn	Zn$^+$	Oxalic	Sodium	NH$_2$OH	Sod. Boro-	-	Sod. Borohydride	
Ton of Tar Sands	-	-	(+NaOH)		(+NaOH)	Acid	Oxalate	(+NaOH)	Hydride	-	-	(6 lbs/Ton)
NaOH in Mixing Sol^n **Wt % on Tar Sand**	-	-	0.08	-	0.08	-	-	0.08	-	-	-	-
Results, wt %												
Froth Composition												
Water	49.1	45.5	50.1	53.4	35.9	51.2	39.5	47.3	42.2	57.0	52.0	54.7
Solids	21.4	34.2	22.0	21.4	15.3	18.0	15.7	15.8	15.9	23.2	21.9	25.0
Oil	29.5	20.3	27.9	25.2	48.8	30.8	44.8	36.9	41.9	19.8	26.1	20.3
Solids/Oil Ratio	0.73	1.69	0.79	0.85	0.31	0.58	0.35	0.43	0.38	1.17	0.84	1.23
Yields (Dry Basis)												
Froth	16.3	15.7	15.6	12.8	13.3	15.1	14.2	15.3	15.0	17.3	14.0	14.9
Water Phase	3.7	6.3	4.9	6.6	4.5	3.4	4.4	3.5	4.3	9.7	11.8	12.0
Sand	80.0	78.0	79.4	80.6	82.1	81.5	81.4	81.2	80.7	73.0	74.2	73.2
Oil Recoveries												
Froth	84.9	55.1	83.9	66.4	91.1	86.8	95.7	94.0	95.8	82.0	85.2	74.1
Water Phase	11.0	21.9	13.1	26.6	8.9	9.8	4.4	4.9	4.2	11.1	13.4	18.1
Sand	4.1	23.0	3.0	7.0	0.0	5.4	0.0	1.1	0.0	6.9	1.4	7.8
Tar Sand Comp^n (Cal^c)												
Oil	10.7	10.2	10.1	10.0	10.8	10.6	10.6	11.0	11.0	8.6	7.9	8.0
Water	3.2	4.0	3.5	3.5	3.3	3.5	3.1	2.7	2.8	11.2	11.5	10.9
Fines	8.6	13.3	10.1	9.4	6.5	7.2	7.4	7.3	7.8	16.0	15.1	16.5
Sand	77.5	72.5	76.4	77.1	79.4	78.7	78.9	79.0	78.4	64.2	65.5	64.6
pH of Water Phase	6.0	4.7	7.6	7.1	10.8	4.9	7.2	8.9	9.4	7.4	9.7	10.0

V3-Table 5

Effect of Addition of Solutions of Additives of Different pH (Hole 11 Tar Sand Containing 7.8 % Oil, 4.1% Water, 15.3% Fines(200-) and 72.8% Sand)

Additive: 2 Wt % Solution Used in Mixing Only ≡ 11.6 lbs/Ton Tar Sand	Ferric Chloride $FeCl_3$	Tannic Acid	Oleic Acid	Distilled Water	Sod. Chloride NaCl	Ferrocyanide $Na_4Fe(CN)_6$	Sod. Sulphite Na_2SO_3	Bicarbonate $NaHCO_3$	Sod. Oleate	Hydrosulphide NaHS	Sod. Silicate Na_2SiO_3	Hydroxide NaOH	Sod. Sulphide Na_2S	Lime: CaO 1% Solution	Calcium Oxide CaO
pH	1.9	3.2	4.6	7.0	7.0	7.3	8.0	8.9	9.5	10.1(1)	11.0(2)	12.5+	12.5+(1)	12.5+	12.5+
Results, Wt %															
Froth Composition(2)															
Water	55.4	52.2	53.8	50.7	50.2	43.7	37.2	35.9	37.8	40.8	37.7	49.6	43.5	51.4	57.8
Solids	30.0	30.9	29.1	31.5	32.7	25.2	21.1	19.6	23.8	17.6	21.4	30.6	18.5	34.5	32.5
Oil	14.6	16.9	17.1	17.8	17.0	31.1	41.7	44.5	38.4	41.6	40.9	19.8	38.0	14.1	9.6
Solids/Oil Ratio	2.06	1.83	1.70	1.78	1.92	0.81	0.51	0.44	0.62	0.42	0.52	1.54	0.49	2.45	3.37
Yields (Dry Basis)															
Froth	11.8	6.8	14.4	14.9	16.4	11.9	10.4	9.3	10.8	8.9	10.0	15.0	8.9	19.7	20.1
Water Phase	8.2	6.2	6.4	6.8	6.5	8.1	10.9	10.5	8.8	11.4	10.1	6.8	13.3	4.0	4.3
Sand	80.0	87.0	79.2	78.3	77.1	80.0	78.7	80.2	80.4	79.7	79.9	78.2	77.8	76.3	75.6
Oil Recoveries															
Froth	49.0	27.4	67.5	65.4	70.5	79.2	84.2	77.6	81.1	78.9	79.3	75.1	72.0	65.7	59.8
Water Phase	25.5	22.0	14.2	14.7	11.6	11.2	13.5	19.5	13.4	18.8	13.9	9.1	26.5	12.3	14.8
Sand	25.5	50.6	18.3	19.9	17.9	9.6	2.3	2.9	5.5	2.3	6.8	15.7	1.5	22.0	25.4
Tar Sand Comp^n (Cal^c)															
Oil	7.5	8.4	7.6	7.8	7.7	7.9	7.9	8.0	7.9	7.6	8.0	7.5	7.9	8.3	7.3
Water	4.3	4.0	4.5	4.2	4.1	4.0	3.8	3.8	4.5	4.4	3.9	4.4	3.9	3.8	4.8
Fines	13.5	8.3	13.7	14.5	15.0	12.0	12.8	11.3	11.2	12.0	11.9	14.5	13.5	16.3	17.8
Sand	74.7	79.2	74.2	73.5	73.2	76.1	75.5	76.9	76.4	76.0	76.2	73.6	74.7	71.6	70.1
pH of Water Phase	3.9	3.9	5.5	5.6	6.4	6.2	7.7	9.7	9.1	10.8	9.4	7.5	9.9	12.5	12.5+

(1) Slight reaction with Brass Pot.
(2) Composite from two aerations.

V3-Table 6

Effect of Addition of Sodium Salt Solutions in Mixing of Different pH, but Equivalent Na Content (Hole 11 Tar Sand Containing 10.8 % Oil, 2.1% Water, 7.1% Fines(200-) and 80.0% Sand)

lbs Sodium Salt (Anhydrous) per Ton of Tar Sands	7.46	10.28	9.42	16.79	4.59	5.57	-------0.0-------			6.21	16.09	4.94	6.59	5.96
Mixing Solution of Sodium Salt containing 0.09 Wt % Na on Tar Sands	Bisulphate $Na_2S_2O_5$	Dichromate $Na_2Cr_2O_7$	Phosphate (Mono) NaH_2PO_4	Metaiodate $NaIO_4$	Chloride $NaCl$	Sulphate Na_2SO_4	Distilled Water			Thiosulphate $Na_2S_2O_3$	Acetate CH_3COONa	Sulphite Na_2SO_3	Bicarbonate $NaHCO_3$	Ferrocyanide $Na_4Fe(CN)_6$
pH	2.6	4.1	4.4	4.6	6.6	6.9	7.0(1)	7.0	7.0	7.6	7.8	8.0	8.3	8.3
Results, Wt %														
Froth Composition(2)														
Water	58.6	56.8	56.2	52.6	43.5	51.4	49.7	48.8	49.8	41.2	49.1	39.0	34.5	46.1
Solids	15.7	14.9	12.6	13.5	20.6	14.9	18.4	17.9	19.3	17.1	14.0	15.0	12.5	12.9
Oil	25.7	28.3	31.2	33.9	35.9	33.7	31.9	33.2	30.9	41.7	36.9	46.0	53.0	41.0
Solids/Oil Ratio	0.61	0.53	0.41	0.40	0.57	0.44	0.58	0.54	0.62	0.41	0.38	0.33	0.24	0.32
Yields (Dry Basis)														
Froth	6.7	7.7	11.2	10.1	16.0	10.4	14.5	15.0	15.8	14.1	13.1	13.1	13.1	13.0
Water Phase	10.7	9.1	6.0	7.4	3.5	6.9	4.2	3.3	33.4	4.0	4.7	4.9	5.2	4.6
Sand	82.6	83.2	82.8	82.5	80.5	82.7	81.3	81.7	80.8	81.9	82.2	82.0	81.7	82.4
Oil Recoveries (Output)														
Froth	38.1	47.4	79.1	66.5	94.4	72.2	85.7	89.1	89.3	93.9	86.7	91.3	92.6	89.2
Water Phase	57.2	43.6	16.5	30.0	2.4	20.4	9.2	5.6	5.8	2.8	8.8	6.7	7.2	6.3
Sand	4.7	9.0	4.4	3.5	3.2	7.4	5.1	5.3	4.9	3.4	4.5	1.9	0.2	4.5
Tar Sand Comp^n (Cal^c)														
Oil	10.7	10.3	10.0	10.6	10.5	10.2	10.5	10.7	10.7	10.4	10.7	10.5	11.2	10.8
Water	2.1	2.3	2.5	1.9	2.3	2.1	2.4	2.1	2.2	2.5	1.9	2.5	1.6	2.0
Fines	6.8	7.0	7.3	6.9	8.8	7.5	8.3	7.8	8.6	7.6	7.2	7.2	6.8	6.9
Sand	80.4	80.4	80.2	80.6	78.4	80.2	78.8	79.4	78.5	79.5	80.2	79.7	80.4	80.3
pH of Water Phase	5.3	5.9	5.5	5.4	5.5	6.7	6.6	6.8	7.0	6.7	7.0	6.7	9.6	7.8

(1) 10 minutes additional stirring before second aeration.

(2) Composite from two aerations.

V3-Table 7

Effect of Addition of Sodium Salt Solutions in Mixing of Different pH, but Same Na Content (Hole 11 Tar Sand Containing 10.8 % Oil, 2.1% Water, 7.1% Fines(200-) and 80.0% Sand)

Mixing Solution of Sodium Salt Containing 0.09 wt % Na on Tar Sand	Phosphate (Di) Na_2HPO_4	Tripolyphosphate $Na_5P_3O_{10}$	Pyrophosphate $Na_4P_2O_7$	Hydrosulphide NaHS (1)	Silicate Na_2SiO_3	Carbonate Na_2CO_3	Aluminate $Na_2OAl_2O_3$	Fusion Product $Na_2OAl_2O_3SiO_2$ (2)	Sulphide Na_2S (1)	Permanganate $NaMnO_4$ (3)	Hydroxide NaOH	Hydroxide NaOH (4)	----- Lime ---- ----- CaO ----- 0.25% Soln	0.50% Soln
lb Sodium Salt (Anhydrous) per Ton of Tar Sands	5.58	5.80	5.22	4.40	4.79	4.16	6.44	4.80	3.06	11.14	3.14	6.18	1.45	2.90
pH	8.8	9.2	9.9	10.5	10.7	11.2	11.9	12.4	12.5+	12.5+	12.5+	12.5+	12.5+	12.5+
Results, Wt %														
Froth Composition[5]														
Water	32.8	41.7	40.5	39.4	38.3	35.8	37.8	36.3	35.5	36.5	39.9	39.9	48.5	35.7
Solids	14.9	11.9	13.2	10.3	12.1	12.9	13.2	9.5	13.3	12.0	11.3	11.1	30.7	48.4
Oil	52.3	46.4	46.3	50.3	49.6	51.3	49.0	54.2	51.2	51.6	48.8	49.0	20.8	15.9
Solids/Oil Ratio	0.29	0.26	0.28	0.20	0.27	0.25	0.27	0.18	0.26	0.23	0.23	0.22	1.47	3.04
Yields (Dry Basis)														
Froth	13.8	13.7	13.5	13.0	13.0	13.2	13.1	12.1	13.1	12.8	12.6	11.5	13.1	25.7
Water Phase	4.7	4.7	4.5	4.7	4.9	4.7	4.4	4.6	5.0	4.8	4.6	4.8	7.1	4.4
Sand	81.5	81.6	82.0	81.3	82.1	82.1	82.5	83.3	81.9	82.4	82.8	83.7	79.8	69.9
Oil Recoveries														
Froth	96.4	94.8	95.2	97.8	94.4	94.1	96.0	93.6	92.8	93.8	93.4	85.5	48.5	58.4
Water Phase	2.8	5.0	4.8	2.2	5.2	5.6	1.6	5.9	6.9	5.7	6.3	9.1	35.8	16.5
Sand	0.8	0.2	0.0	0.0	0.4	0.3	2.4	0.5	0.3	0.5	0.3	5.4	15.7	25.0
Tar Sand Comp^n (Cal^c)														
Oil	10.9	11.3	10.8	11.3	10.8	11.1	10.5	10.8	10.9	10.8	10.6	10.7	10.6	10.6
Water	1.8	1.7	2.1	2.4	1.4	1.6	2.0	1.5	2.3	2.1	2.2	3.1	2.5	2.5
Fines	7.3	6.8	6.8	6.6	6.9	6.6	6.9	5.7	6.8	6.4	6.2	5.7	10.7	21.4
Sand	80.0	80.2	80.3	79.7	80.9	80.7	82.0	80.6	80.0	80.7	81.0	80.5	76.2	65.5
pH of Water Phase	5.9	8.7	9.2	8.9	9.9	10.3	10.4	10.3	10.4	10.5	10.7	12.3	10.6	12.5

(1) Slight reaction with Brass Pot.
(2) From fusing lens clay and sodium hydroxide in a 1:1 wt ratio and leaching of 59% of the fused product with water. The remainder being unreacted clay.
(3) Not entirely in solution.
(4) Some loss due to tendency to bubble over.
(5) Composite from two aerations.

V3-Table 8

Effect of Surfactants Class with pH Control on a Hole 11 Tar Sand

Mixing Solution (lbs/ton) ---------- Sodium Hydroxide (0.5) + Sodium Tripolyphosphate (1.0) ----------

Surfactant (0.1 wt % on Tar Sand)	Blank	Blank	Pluronic L 61*	Pluronic F 68*	Pluronic L 44*	Yarmor F Pine Oil	Di Na Ethylene Tetraacetate diamine	Cresylic Acid	Ethylene Diamine	Hyamine (#2389)	d1 Alanine	Na Carboxy Methyl Cellulose	Perfluoro Hexane	Anti-Form A - Silicone
Surfactant Class	-	-	1	1	1	1	2	2	3	3	4	5	6	7
Results, Wt %														
Froth Composition														
Water	45.9	34.6	34.4	35.9	28.2	29.3	31.8	33.7	34.9	53.5	32.6	30.5	34.1	43.1
Solids	38.4	30.9	24.8	26.1	31.6	35.9	29.3	32.2	26.6	26.3	32.1	38.3	35.2	26.6
Oil	15.7	34.5	40.9	38.0	40.1	34.8	38.9	34.0	38.5	20.3	35.3	31.2	30.7	30.3
Solids/Oil Ratio	2.43	0.89	0.61	0.69	0.79	1.03	0.75	0.95	0.75	1.29	0.91	1.22	1.14	0.88
Yield (Dry Basis)														
Froth	13.7	13.7	11.7	12.7	14.9	15.9	14.9	15.2	13.2	9.6	14.8	13.6	14.4	9.8
Water Phase	3.7	5.9	6.4	6.2	5.9	5.2	5.9	5.0	6.1	6.5	5.3	6.8	5.7	6.6
Sand	82.6	80.4	81.9	81.1	79.2	78.9	79.2	79.8	80.7	83.9	79.9	79.9	79.9	83.5
Oil Recoveries														
Froth	49.2	82.0	83.8	88.4	88.1	89.7	91.9	89.2	86.3	55.6	82.4	71.5	81.1	62.1
Water Phase	3.9	7.1	8.4	6.3	6.5	4.2	3.5	4.5	9.5	14.4	4.1	8.6	7.4	12.7
Sand	46.9	10.9	7.8	5.3	5.4	6.1	4.7	6.3	3.3	30.0	13.5	19.9	11.4	25.1
Tar Sand Comp^n (Cal^c)														
Oil	7.4	8.3	8.2	8.0	8.9	8.2	8.7	8.3	8.1	6.9	8.8	8.0	7.7	7.9
Water	7.8	5.9	5.8	5.7	6.4	6.3	6.0	6.2	6.5	7.8	6.6	6.5	6.7	6.7
Fines	12.1	11.1	9.5	10.2	11.1	12.1	11.3	11.4	9.4	10.0	11.2	12.3	11.9	9.5
Sand	72.7	74.7	76.6	76.1	73.6	73.5	74.1	74.1	76.1	75.3	73.5	73.1	73.7	76.0
pH of Water Phase	4.3	7.4	7.6	7.8	7.7	7.8	7.2	7.4	9.3	7.2	7.3	7.0	7.3	7.4

* % Polyoxyethylene (hydrophilic unit) in polypropylene hydrophobic base was 10 for L61, 80 for F68, and 40 for I44 of low M Wt Base 1200:1750.

V3-Table 9

Effect of Nonionics and Silicones of Different Molecular Weights on Area B and Hole 11 (with pH Control Tar Sand

Sand	**Area B**						**Hole 11**				
Mixing Solution (lb/ton)	**Distilled Water**						**Na TPP(2.90)(1)**				
Surfactant (Wt % on Tar Sand)											
	-	**Span "80"**	**Lard Oil**	**Castor Oil**	**Anti-Foam Q**	**Silicone-200-350**	-	**Silicone(0.1) 0.65**	**10**	**350**	**1000**
Class	-	**1**			**7**		-	**7**			
Molecular Weight	-	-	-	-	-	-	-	162	1100	18,000	27,500
Results, Wt %											
Froth Composition											
Water	43.8	32.3	32.2	36.3	40.7	38.7	38.1	46.6	35.9	32.3	38.0
Solids	17.7	13.7	15.0	14.2	11.1	11.8	14.3	16.4	13.3	7.8	11.0
Oil	38.5	54.0	52.8	49.5	48.2	49.5	47.6	37.1	50.8	59.9	51.1
Solids/Oil Ratio	0.46	0.25	0.29	0.29	0.23	0.24	0.30	0.44	0.26	0.13	0.22
Yields (Dry Basis)											
Froth	17.9	15.8	16.8	16.4	14.2	14.6	13.8	15.5	13.6	12.3	13.2
Water Phase	3.0	3.1	2.9	3.0	4.1	4.3	4.4	3.6	4.4	5.2	4.6
Sand	79.2	81.1	80.3	80.6	81.7	81.1	81.7	80.8	81.9	82.5	82.2
Oil Recoveries											
Froth	97.0	97.2	96.3	95.5	89.3	88.5	95.1	96.3	95.2	93.4	95.1
Water Phase	2.7	1.9	2.7	2.9	9.3	9.0	4.9	3.7	4.8	6.6	4.9
Sand	0.3	0.9	1.0	1.6	1.4	2.5	0.0	0.0	0.0	0.0	0.0
Tar Sand Composition (cal^c)											
Oil	12.0	12.4	13.0	12.8	12.2	12.7	10.8	10.8	11.0	11.3	11.1
Water	4.9	4.4	4.2	3.8	5.0	4.4	2.5	2.9	2.3	2.1	2.6
Fines	7.8	5.8	6.0	6.0	5.3	5.6	6.9	7.7	6.6	5.7	6.2
Sand	75.3	77.4	76.8	77.4	77.4	77.2	79.8	78.5	80.0	80.9	80.1
pH of Water Phase	7.8	7.2	7.5	7.6	7.5	7.4	7.8	7.7	7.7	7.7	7.7

(1) Sodium tripolyphosphate.

V3-Table 10

Effect of Amphoteric Surfactants with pH Control on a very Low Oil-High Fines Hole 21A and High Oil Hole 11

Tar Sand	Hole 21A(Low Oil)				Hole 11		
Mixing Solution (lb/ton)		NaOH(1.57)	NaOH(3.14)	NaOH(6.28)	D.W.		2 Na_2SiO_2(1.87)
Surfactant		Di Sodium Tetra-Acetate Diamine[1]				$C_{18}H_{37}NH(CH_2)_3SO_3Na$ 635-13A	
Class		4				4	
Results							
Froth Composition							
Water	54.2	55.0	53.7	42.1	45.0	38.4	27.9
Solids	40.2	36.7	31.7	38.3	19.1	27.6	11.8
Oil	5.6	8.3	14.6	19.6	35.9	33.9	60.4
Solids/Oil Ratio	7.07	4.40	2.17	1.95	0.53	0.81	0.20
Yields (Dry Basis)							
Froth	11.9	4.7	2.9	2.5	13.5	6.5	6.0
Water Phase	43.9	58.8	57.2	48.9	3.9	5.2	9.6
Sand	44.4	36.5	39.9	48.5	82.6	88.3	84.4
Oil Recoveries							
Froth	40.9	37.8	29.0	24.4	81.7	33.2	47.6
Water Phase	9.5	18.2	51.5	66.2	9.8	22.3	50.3
Sand	49.6	44.0	19.5	9.4	8.5	44.4	2.0
Tar Sand Composition (cal^c^)							
Oil	3.3	2.1	2.9	3.2	10.4	10.3	10.1
Water	8.5	8.3	6.7	8.2	3.2	3.9	3.9
Fines	49.2	57.0	53.7	44.4	7.3	5.5	5.1
Sand	39.0	32.6	36.7	44.3	79.1	80.2	80.9
pH of Water Phase	6.3	8.5	9.4	11.9	6.3	7.9	10.2

(1) Versene.

V3-Table 11

Effect of HLB Surfactants with Area B and Hole 11 Tar Sand

Tar Sands	**Area B**						**Hole 11**					
Surfactant		**HLB Series**						**HLB Series**				
#		**2**	**6**	**10**	**14**	**18**		**2**	**6**	**10**	**14**	**18**
Results												
Froth Composition												
Water	43.8	35.3	36.6	44.3	35.9	37.8	46.8	54.4	56.4	68.8	69.7	64.3
Solids	17.7	17.2	14.0	11.3	11.8	13.7	32.2	30.0	26.1	17.0	18.3	18.9
Oil	38.5	47.5	49.4	44.4	52.3	48.5	21.0	15.6	17.5	14.2	12.1	16.8
Solids/Oil Ratio	0.46	0.36	0.28	0.26	0.23	0.28	1.53	1.93	1.49	1.20	1.51	1.13
Yields (Dry Basis)												
Froth	17.9	18.1	15.6	14.2	14.1	17.5	10.4	7.9	7.9	4.8	4.2	5.4
Water Phase	3.0	2.7	3.2	3.6	4.0	3.5	3.3	3.6	5.8	6.8	6.7	8.4
Sand	79.2	79.3	81.2	82.2	81.9	79.0	86.4	88.5	86.4	88.4	89.1	86.3
Oil Recoveries												
Froth	97.0	97.7	94.5	87.5	88.3	99.3	46.2	35.5	36.9	27.2	22.1	31.6
Water Phase	2.7	1.3	3.5	6.7	7.9	0.7	2.7	4.0	15.0	32.8	35.5	39.2
Sand	0.3	1.0	2.0	5.8	4.0	0.0	51.2	60.5	48.1	39.9	42.4	29.2
Tar Sand Composition (cal^c)												
Oil	12.0	12.9	12.2	12.2	12.4	13.1	8.2	7.0	8.0	7.4	7.0	7.4
Water	4.9	4.7	5.3	5.5	5.1	4.8	7.6	7.9	6.8	7.5	7.5	6.8
Fines	7.8	6.9	5.9	5.3	5.3	6.9	8.6	7.8	8.6	6.3	6.0	7.5
Sand	75.3	75.4	76.6	77.0	77.2	75.2	75.6	77.3	76.7	78.7	79.4	78.3
pH of Water Phase	7.8	7.7	7.1	7.6	7.8	7.7	5.9	6.0	6.1	5.6	3.9	4.0

HLB's are mixtures of span and tween.

V3-Table 12

Effect of HLB Surfactants with pH Control and a Hole 11 Tar Sand

Tar Sand	Hole 11 (High Oil)										
Mixing Solution (lb/ton)	D.W.	Sodium Silicate 2 Na_2OSiO_2(1.87)									
Surfactant	-	-	HLB Series[1]								
#	-	-	2	4	6	8	10	12	14	16	18
Results											
Froth Composition											
Water	45.0	30.3	33.2	30.2	31.8	30.1	32.0	34.2	33.7	33.0	26.7
Solids	19.1	177	15.2	18.3	17.3	13.1	13.9	12.6	14.4	15.2	18.2
Oil	35.9	52.0	51.6	51.5	50.9	56.8	54.2	53.2	51.9	51.8	55.1
Solids/Oil Ratio	0.53	0.34	0.30	0.36	0.34	0.23	0.26	0.24	0.28	0.29	0.33
Yields (Dry Basis)											
Froth	13.5	13.7	12.1	14.0	12.8	12.5	12.8	12.8	12.8	12.8	14.4
Water Phase	3.9	4.1	4.3	4.3	4.6	4.5	4.2	5.8	3.7	4.1	4.1
Sand	82.6	82.1	83.5	81.7	82.6	83.0	83.1	81.4	83.5	83.1	81.6
Oil Recoveries											
Froth	81.7	91.5	86.3	91.8	87.9	88.7	91.6	92.4	93.1	90.6	94.9
Water Phase	9.8	5.5	7.8	6.3	7.5	6.6	5.8	5.0	3.1	5.9	4.2
Sand	8.5	3.0	5.9	1.9	4.6	4.7	2.6	2.6	3.8	3.5	0.9
Tar Sand Composition (cal^{c})											
Oil	10.4	10.9	10.5	10.9	10.5	11.1	10.8	10.9	10.3	10.6	11.0
Water	3.2	3.1	3.4	2.9	3.3	3.0	2.8	3.3	4.0	3.1	2.8
Fines	7.3	6.8	6.0	7.1	6.8	5.9	5.9	7.4	5.9	6.2	7.0
Sand	79.1	79.3	80.0	79.1	79.4	80.0	80.5	78.4	79.8	80.1	79.2
pH of Water Phase	6.3	9.0	9.0	9.2	9.1	9.1	9.0	9.0	9.0	9.1	9.1
Zeta Potential of (mv)	13.7	12.3	13.3	14.3	14.3	11.8	13.0	13.4	11.3	14.1	13.5

(1) HLB's are mixtures of span and tween.

V3-Table 13

Complexing Chemical Addition to Beaver River Tar Sands

(Bench Unit Feed - Run No. 6 Tar Sand, 0.005 wt % addition of complexing agent, and 0.06 wt % NaOH for pH adjustment)

Complexing Agent	**None (1)**	**Nitrilotri Acetic Acid**	**Versenex 80**	**Versene Fe-3**	**Versenol 120**	**Ethylene Diamine Tetra Acetate**	**Sodium Citrate**
No Aeration Froth							
Solids/Oil Ratio	0.22	0.19	0.18	0.20	0.13	0.20	0.20
Water/Oil Ratio	0.48	0.45	0.40	0.45	0.40	0.45	0.47
Oil Recovery, wt %	89.3	85.8	84.7	81.9	85.0	89.6	86.8
No + 1st Aeration Froths							
Solids/Oil Ratio	0.24	0.20	0.20	0.22	0.16	0.23	0.26
Water/Oil Ratio	0.55	0.49	0.49	0.49	0.49	0.55	0.58
Oil Recovery, wt %	93.5	89.9	93.6	93.4	92.6	94.3	93.6
No + 1st + 2nd Aeration Froths							
Solids/Oil Ratio	0.27	0.26	0.24	0.25	0.19	0.29	--
Water/Oil Ratio	0.56	0.54	0.57	0.55	0.58	0.97	--
Oil Recovery, wt %	96.3	94.0	94.6	95.3	95.6	94.7	93.6
Oil Loss to Water Phase	3.6	5.3	4.8	4.0	3.8	4.4	4.9
Oil Loss in Sand	0.1	0.6	0.6	0.7	0.6	0.9	1.5
Water Phase							
Hydroxy Ions pH_2	10.2	9.8	9.5	9.5	9.3	9.6	9.5
Zeta Potential $2P_1$	36	53	37	46	33	39	39
Zeta Potential $2P_2$	56	49	42	46	50	45	47
Conductance C_2	2140	2040	1564	1560	1496	1700	1490

(1) 0.12 Wt % NaOH was used.

V3-Table 14

Complexing Chemical Addition to Beaver River Tar Sands

(Intermediate Tar Sands, 0.05 Wt % addition of complexing agent, and 0.06 Wt % NaOH for pH adjustment)

Complexing Agent	**None (1)**	**Nitrilotri Acetic Acid**	**Versenex 80**	**Versene Fe-3**	**Ethylene Diamine Tetra Acetate**	**4 p Nitro Phenyl Azo Resorcinol**	**Titan Yellow**
No Aeration Froth							
Solids/Oil Ratio	0.25	0.23	0.21	0.23	0.23	0.11	0.20
Water/Oil Ratio	0.72	0.46	0.40	0.40	0.41	0.60	0.47
Oil Recovery, Wt %	85.9	82.2	85.4	90.0	81.4	82.3	81.5
No + 1st Aeration Froth							
Solids/Oil Ratio	0.28	0.26	0.24	0.27	0.25	0.16	0.24
Water/Oil Ratio	0.70	0.52	0.47	0.49	0.45	0.68	0.56
Oil Recovery, Wt %	90.4	90.1	89.3	90.0	89.3	94.1	95.4
No + 1st + 2nd Aeration Froth							
Solids/Oil Ratio	0.28	-	0.30	-	0.31	-	0.29
Water/Oil Ratio	0.71	-	0.59	-	0.51	-	0.65
Oil Recovery, Wt %	90.4	90.1	91.2	90.0	90.2	94.1	94.0
Oil Loss to Water Phase	8.8	8.0	8.4	10.1	8.8	4.9	4.5
Oil Loss in Sand	0.8	1.9	0.3	0.0	1.0	1.0	1.5
Water Phase							
Hydroxyl Ions pH_2	10.2	9.5	12.2	9.7	9.4	9.7	9.6
Zeta Potential, ZP_1	43	43	62	41	50	40	42
ZP_2	66	65	38	62	62	45	47
Conductance C_2	2,040	2,312	10,880	2,108	2,244	1,360	1,768

(1) 0.12 Wt % NaOH was used.

V3-Table 15

Complexing Chemical Addition to Beaver River Tar Sands

(Bench Unit Feed - Run No. 6 Tar Sand, 0.05 Wt % additive of complexing agent, and 0.06 Wt % NaOH for pH adjustment)

Complexing Agent	**None (1)**	**Nitriiotri Acetic Acid**	**Versenex 80**	**Versene Fe-3**	**Versenol 120**	**Ethylene Diamine Tetra Acetate**	**Sodium Citrate**	**Picro Lonic Acid**	**Tetra-Hydroxy Anthra Quinone**	**7 Iodo Quinoline 5 Sulphuonic Acid**
No Aeration Froth										
Solids/Oil Ratio	0.22	0.07	0.16	0.18	0.17	0.21	0.18	0.05	0.11	0.19
Water/Oil Ratio	0.48	0.45	0.20	0.40	0.31	0.53	0.44	0.41	0.61	0.45
Oil Recovery, wt %	89.3	87.8	85.4	83.9	85.1	84.3	88.5	88.7	83.0	80.3
No + 1st Aeration Froths										
Solids/Oil Ratio	0.24	0.09	0.18	0.20	0.19	0.23	0.20	0.08	0.19	0.22
Water/Oil Ratio	0.55	0.51	0.29	0.46	0.38	0.62	0.57	0.54	0.70	0.56
Oil Recovery, wt %	93.5	94.0	94.0	94.9	94.4	90.3	93.9	95.5	92.2	92.1
No + 1st + 2nd Aeration Froths										
Solids/Oil Ratio	0.27	0.14	0.20	0.26	--	0.27	--	--	0.23	0.27
Water/Oil Ratio	0.56	0.52	0.32	0.60	--	0.73	--	--	0.83	0.63
Oil Recovery, wt %	96.3	95.9	95.5	95.4	94.4	93.3	94.0	95.5	94.4	93.9
Oil Loss to Water Phase	3.6	3.5	4.0	4.1	4.8	5.3	5.3	3.4	4.7	5.2
Oil Loss in Sand	0.1	0.7	0.5	0.5	0.9	1.4	0.7	1.1	0.9	0.9
Water Phase										
Hydroxyl Ions pH_2	10.2	9.3	9.8	9.7	9.6	9.4	9.6	9.2	9.4	9.5
Zeta Potential ZP_1	36	41	37	35	42	35	38	38	40	40
Zeta Potential ZP_2	56	52	47	48	45	43	50	46	45	--
Conductance C_2	2140	1700	1904	1496	1632	1565	1836	1700	1360	--

(1) 0.12 Wt % NaOH was used.

V4

SAND REDUCTION SEPARATIONS

V4-Table 1

Effect of Water Addition (or Shear) on Sand Reduction in Mixing

Mortar and Pestle Experiments

(Tar Sand, No. 2A, contained 13 wt % oil and 7 wt % water)

Experiment Number	**2A00**	**2A01**	**2A02**	**2A03**	**2A04**	**2A05**	**2A13**	**2A15**	**2A26**	**2A17**
Conditions										
Temperature, °F	70-75									
Total water, Wt %(1)	50	50	100	150	75	75	75	400	300	75
Mixing Time, min	10	5	5	5	5	10	6	5	5	5(5)
Results, Wt %										
Oil Conc. Yield(1)	46.0	20.1	35.6	37.8	19.8	32.9	34.0	37.0	40.8	23.7
Sand Yield(1)	54.0	79.9	64.4	62.2	80.2	67.1	66.0	63.0	59.2	76.3
Oil in Conc.(2)	29.0	50.1	39.0	37.5	58.4	44.1	41.3	34.5	64.8	49.0
Oil in Sand(2)	-	4.1	-(4)	-(4)	2.2	-(4)	0	-	0	1.4
Water in Oil Conc.	-	-	20.5	20.3	25.0	23.8	-	-	-	-
Wt Balance	100	98	100	100	99	101	99	92	100	93
Oil Recovery(3) (est.)	95	77	-- (~100)--		88	(~100)	100	(~90)	100	92
% of Total Solids Removed	63	90	76	74	93	79	78	73	70	89

(1) On tar sands (dry output basis)
(2) Obtained from ash determinations
(3) Based on ash values on total sand recovered
(4) Very clean sand, oil content presumably 0 or <0.5 wt %
(5) Progressive water addition.

V4-Table 2

Effect of Water Addition (or Shear) on Sand Reduction in Mixing

Mortar and Pestle Experiments

(Tar Sand, No. 3, contained 18 wt % oil and 2 wt % water)

Experiment Number	**301**	**302**	**304**	**305**	**306**	**303**
Conditions						
Temperature, °F	70-75					
Total water, Wt %(1)	50	75	100	150	200	400
Mixing time, min	5					
Results, Wt %						
Oil Conc. Yield(1)	72.1	63.2	62.8	90.6	73.2	80.4
Sand Yield(1)	27.9	36.8	37.2	9.4	26.8	19.6
Oil in Conc.(2)	24.2	29.2	26.5	19.5	23.8	24.0
Oil in Sand (2)	-(4)	0	-(4)	-(4)	-(4)	-(4)
Wt Balance	96	99	97	98	100	98
Oil recovery(3) (est.)	(~100)	100	(~100)			
% of Total Solids Removed	34	45	45	11	32	24

(1) On tar sands (dry output basis)
(2) Obtained from ash determinations
(3) Based on ash values on total sand recovered
(4) Very clean sand, oil content presumably 0 or <0.5 wt %.

V4-Table 3

Effect of Water Addition (or Shear) and Temperature on Sand Reduction in Mixing

Mortar and Pestle Experiments

(Tar Sand, No. 4, contained 15 wt % oil and 5 wt % water)

Experiment Numbers	**401**	**402**	**408**	**403**	**404**	**405**	**406**	**407**	**409**	**410**
Conditions										
Temperature, °F(1)	70-75							96	50	37
Total water, Wt %(2)	50	75	75	100	150	200	400	75		
Mixing time, min	5									
Results, Wt %										
Oil Conc. Yield(2)	42.2	43.0	46.9	42.6	57.0	51.5	54.9	37.9	41.3	29.3
Sand Yield(1)	57.8	57.0	53.1	57.4	43.0	48.5	45.1	62.1	58.7	70.7
Oil in Conc.(3)	33.5	34.6	33.8	34.9	28.2	32.8	28.9	39.6	36.8	49.5
Oil in Sand(3)	-	-(5)	0	-(5)	-(5)	-(5)	-(5)	0	0	0.4
Wt Balance	97	98	97	98	100	96	98	96	99	100
Oil recovery(4) (est.)	(~100)		100		(~100)			100	100	98
% of Total Solids Removed	69	68	63	68	51	58	54	74	70	83

(1) Average
(2) On tar sands (dry output basis)
(3) Obtained from ash determinations
(4) Based on ash values on total sand recovered
(5) Very clean sand, oil content presumably 0 or <0.5 wt %.

V4-Table 4

Effect of Water Addition (or Shear) and Temperature on Sand Reduction in Mixing

Mortar and Pestle Experiments

(Tar Sand, No. 5, contained 16 wt % oil and 1 wt % water)

Experiment Number	**501**	**504**	**502**	**503**	**508**	**505**	**506**	**509**	**507**	**510**
Conditions										
Temperature, °F(1)	70-75						110	135	140	150
Total water, Wt %(2)	50	75	100	150	400	75	75			
Mixing time, min	5					10	5			
Results, Wt %										
Oil Conc. Yield(2)	74.6	80.8	72.1	96.7	99.6	78.0	39.7	58.5	45.4	41.0
Sand Yield(2)	25.4	19.2	27.9	3.3	0.4	22.0	60.3	41.5	54.6	59.0
Oil in Conc.(3)	22.6	20.9	24.4	17.1	14.5	20.5	-	-	29.5	33.5
Oil in Sand(3)	-(5)	-(5)	-(5)	-(5)	-(5)	-(5)	-	1.4	2.6	1.9
Water in Oil Conc.	23.5	20.3	19.6	21.5	24.2	25.4	-	-	-	-
Wt Balance	96	96	96	98	98	96	92	92	100	94
Oil recovery(4) (est.)	(~100)						-	96	90	92
% of Total Solids Removed	31	23	34	4	1	26	72	50	63	69

(1) Average
(2) On tar sands (dry output basis)
(3) Obtained from ash determinations
(4) Based on ash values on total sand recovered
(5) Very clean sand, oil content presumably 0 or <0.5 wt %.

V4-Table 5

Effect of Water Addition (or Shear) on Sand Reduction in Mixing

Mortar and Pestle Experiments

(Tar Sand, No. 6, contained 16 wt % oil and 6 wt % water)

Experiment Numbers	**601**	**605**	**602**	**612**	**603**	**604**	**606**	**620**	**615**
Conditions									
Temperature, °F	70-75								
Total water, Wt %(1)	80(5)	50	62.5	75	100	150	200	300	400
Mixing time, min	10	5	10	5					
Results, Wt %									
Oil Conc. Yield(1)	28.2	51.8	39.7	38.8	38.2	50.4	55.0	50.0	48.7
Sand Yield(1)	71.8	48.2	60.3	61.2	61.8	49.6	45.0	50.0	51.3
Oil in Conc.(2)	59.7	32.6	43.5	41.5	43.9	32.6	31.8	32.7	32.5
Oil in Sand(2)	-(4)	-(4)	-(4)	0	-(4)	-(4)	-(4)	0	-(4)
Water in Oil Conc.	23.8	26.9	24.8	25.0	25.9	20.0	22.5	-	-
Oil in Oil Conc.	59.9	32.6	63.3	42.5	44.0	32.5	31.8	-	-
Wt Balance	101	99	101	96	100	102	100	100	92
Oil recovery(3) (est.)	(~100)			100	(~100)			100	(~92)
% of Total Solids Removed	87	58	73	73	73	59	54	60	61

(1) On tar sands (dry output basis)
(2) Obtained from ash determinations
(3) Based on ash values of total sand recovered
(4) Very clean sand, oil content presumably 0 or <0.5 wt %
(5) Progressive water addition.

V4-Table 6

Effect of Temperature on Sand Reduction by Shear Only

Mortar and Pestle Experiments

(Tar Sand, No. 6, contained 16 wt % oil and 6.0 wt % water)

Experiment Number	**609**	**610**	**611**	**613**	**614**	**616**	**617**	**618**	**619**
Conditions									
Temperature, °F(1)	110	130	90	55	40	125	140	76	150
Total water, Wt %(2)	75								
Mixing time, min	5								
Results, Wt %									
Oil Conc. Yield(2)	47.2	43.5	49.2	30.7	25.8	54.9	51.2	42.5	47.0
Sand Yield(2)	52.8	56.5	50.8	69.3	74.2	45.1	48.8	57.5	53.0
Oil in Conc.(3)	-	37.4	31.5	53.8	53.8	28.5	30.5	38.2	32.2
Oil in Sand(3)	-(4)	1.5	0	0.5	0.8	-	0.6	-(4)	-(4)
Water in Conc.	18.8								
Wt Balance	99	96	98	95	98	98	98	100	98
Oil recovery(5) (est.)	-	94	100	97.5	95	-	98	(~100)	-
% of Total Solids Removed	63.6	66	61	83	86	54	58	70	63

(1) Average
(2) On tar sand (dry output basis)
(3) Obtained from ash determinations
(4) Very clean sand, oil content presumably 0 or <0.5 wt %
(5) Based on ash values of total sand recovered.

V4-Table 7

Effect of "Clay" on Sand Reduction (Motar and Pestle Experiments) (Tar Sand, No. 11, Contained 15 Wt % Oil and 6 Wt % Water)

Experiment Number	**1103**	**1105**	**1102**	**1106**	**1104**	**1107**	**1101**
Conditions							
Clay(1) addition, Wt %	0	16	27	35	40	41	54
Total water, Wt %	74	79	80	84	90	137	86
Temperature, °F	70-80						
Mixing time, min	2						
Results, Wt %							
Oil Conc. Yield(2)	23.6	21.3	19.4	16.0	11.8	16.0	8.2
Clay Yield(2)	1.2	14.6	15.4	20.2	25.0	25.2	30.1
Sand Yield(2)	75.2	64.1	65.2	63.8	63.2	58.8	61.7
Oil Balance							
Oil in oil conc.	100	100	98	73	72	81	60
Oil in clay	0	0	0	12	4	7	0
Oil in sand	0	0	2	16	24	12	40
Ash on oil conc.	32	46	37	50	31	54	19
Wt Balance	93	93	98	96	99	95	94

(1) Clay obtained from a mined pocket (dry basis i.e., oven dried which ashes at 92)

(2) On total feed (dry output basis).

V4-Table 8

Effect of Addition of Water and Fluid Coke on Sand Reduction in Mixing[3]
Mortar and Pestle Experiments. Tar Sand, No. 2A, contained 13 Wt % Oil and 7 Wt % Water

Experiment Number	2A20	2A21	2A22	2A07	2A23	2A18	2A19	2A24
Conditions								
Fluid Coke addition, Wt %[1]	5	5	5	10	25	25	25	25
Temperature, °F	70-75							
Total water, Wt %[1]	50	100	200	75	50	100	100	200
Mixing time, min	5							
Results, Wt %								
Oil Conc. Yield[1] (less coke)	3.8	37.9	37.7	35.9	19.5	30.5	33.1	34.4
Sand Yield[1]	96.2	62.1	62.3	64.1	80.5	69.5	66.9	65.6
Wt Balance	95	100	100	100	96	100	99	101
Oil recovery[2] (est.)	26	100	100	(~100)	89	100	100	100
% of Total Solids Removed	-	72	72	75	-	81	78	76

(1) On tar sand (dry output basis)
(2) Obtained from ash determinations
(3) These results may be compared with those in Appendix Table 1 for no water addition.

V4-Table 9

Effect of Addition of Water and Fluid Coke , and Temperature on Sand Reduction in Mixing(3) (Mortar and Pestle Experiments) (Tar Sand, No. 3, contained 2 wt % Water and 18 wt % Oil)

Experiment Number	**308**	**307**	**313**	**309**	**310**	**311**	**312**
Conditions							
Fluid Coke addition, Wt %(1)	5	25					
Temperature, °F	73	73	70	73	115	128	127
Total water, Wt %(1)	100	50	100	200	50	100	200
Mixing time, min	5						
Results, Wt %							
Oil Conc. Yield(1) (less coke)	65.7	56.3	50.8	53.7	55.2	32.5	28.1
Sand Yield(1)	34.3	43.7	49.2	46.3	44.8	67.5	71.9
Wt Balance	97	95	98	97	96	96	97
Oil recovery(2) (est.)	100	100	100	100	100	100	100
% of Total Solids Removed	42	54	60	57	55	83	88

(1) On tar sand (dry output basis)
(2) Obtained from ash determinations
(3) These results may be compared with those in Appendix Table 2 for no coke addition.

V4-Table 10

Mechanical(1) Batch Mixing Operations (Tar Sand, No.8 contained 5 wt % water and 15 wt % Oil Average results for condition: 65 and 110 wt % water, 70 °F, 3 1/2 and 7 1/2 min mixing time)

Type of Mixer(2)	Speed Rev/min	Number of Experiments	Tar Sand Charge g	Weight Percent Water in Oil Phase	 Oil in Oil Phase	 Oil Recovery	 Solids Removed
Mixers that gave poor agglomeration							
Grease	35	6	500	12	39	92	68
Hobart Mixer	60	1	500	12	27	81	61
Hobart Beater	62	5	300	13	32	88	65
Tumbler	60	1	400	-	26	75	63
Mixers that gave good agglomeration							
Mortar and Pestle	60	7	25 and 200	20	30	99.8	63
"Full View" Mixer							
(a) Square Helix	60	9	400	14	34	97.3	67
(b) Ribbon	60	5	400	15	35	98.6	67
Kneader	20 and 30	4	640	14	36	94	69
Pug Mill	120	1	2500	-	31	95	59

(1) Agglomerate screened from sand using 20 mesh "submerged" sieve in an ASTM shaker.

(2) Dimensions and direction of rotation are shown in Appendix Figures 3 and 4.

V4-Table 11

Summary of Experimental Results with Continuous Helix

Run Number (Element)(1)	Tar Sands(2) lb/hr (No.)	Bath Temperature, °F			Wt % Oil in(3) Oil Phase	Wt % Sand(4) Reduction
		1	2	3		
1 (H)	25 (8)	32	32	32	27.7	51.0
2 (H)	25 (8)	125	50	32	30.3	56.9
3 (H)	25 (8)	70	70	70	32.3	60.6
4 (H)	35 (11)	70	70	70	60.0	88.4
5-13 (H and R)	--------------- Capacity - Speed Tests (See Appendix Figures) ---------------					
14 (R)	30 (11)	70	70	70	48.1	81.0
15 (R)	30 (11)	160	70	32	41.8	75.6
16 (R)	30 (11)	150	70	32	39.4	73.1
" (2nd pass)	30	150	70	32	53.8	85.0
17-19 (H)	---------------------------- Screening Speed Tests ------------------------					
20 (H)	30 (11)	70	70	70	38.2	71.7
21 (H)	30 (8)	70	70	70	28.5	52.9
"	30 (9)	70	70	70	45.4	82.7

(1) Mixing Element: H = solid helix; R = ribbon (same as for the Full View Mixer, Appendix Figure 4).

(2) Water added was about 75-100 wt % on tar sands feed.

(3) About 99 wt % oil recovery in oil phase.

(4) Oil in sand was not measured as sand was so clean. Spot samples ashed at 99.7%.

V5

SOLVENT DILUTION CLEAN UP OF OIL

V5-Table 1

Effect of Temperature, pH, and Sodium Salts on Water-Wet Solids Removal from Good Quality Froth by Solvent Dilution with 1:1 Xylene Wt. Ratio (Froth Composition wt %: Water -23, Solids -5, and Oil -72)

(Froth Composition Wt%: water - 23, solids - 5, and oil - 72)

Separation Conditions													
Temperature, °F	75	115	155	195	---------- 155 ----------								
Chemical Addition in													
Mixing - Type	-	-	-	-	-----	NaOH	-----	HCl	---	Na_2CO_3	--Na_2SiO_3--		$Na_5P_1O_{10}$
- % on Froth	-	-	-	-	0.1	0.4	0.5	0.1	0.1	0.2	--------0.1---		0.6
Water - Type	-	-	-	-	-	-	-	-	-	-	-	$Na_2.SiO_3$	-
- % on Froth	-	-	-	-	-	-	-	-	-	-	-	0.0006	-
pH (Average) of water phase	7.3	7.0	7.0	7.0	9.0	10.7	12.5	3.0	8.0	9.2	8.8	9.4	9.3
Results, Wt% on Total													
Solids Removal in													
10 minutes	16	20	16	16	17	19	10	20	22	23	18	30	10
30 minutes	19	24	20	20	20	22	13	25	25	29	20	40	20
60 minutes	22	27	22	24	29	27	16	29	26	32	24	45	27
120 minutes	24	28	24	24	33	29	19	33	28	35	30	49	33
180 minutes	27	30	26	24	36	30	20	35	29	39	33	51	36
300 minutes	28	31	27	25	39	32	20	38	34	41	35	52	40
Solids remaining in O.P.	19	12	14	-	21	12	25	-	18	18	19	17	14
Solids in Sludge (Diff.)	53	57	59	-	40	56	55	-	48	41	48	31	45
Oil Loss with Solids in													
10 minutes	0.3	0.6	0.4	0.3	0.7	0.3	0.2	0.3	0.4	0.4	0.4	0.3	0.05
30 minutes	0.3	0.6	0.6	0.8	0.7	0.4	0.2	0.4	0.5	0.5	0.4	0.3	0.05
60 minutes	0.3	0.7	0.7	2.2	0.9	0.4	0.2	0.4	0.5	0.5	0.4	0.4	0.1
120 minutes	0.3	0.8	0.7	2.2	1.0	0.5	0.2	0.5	0.6	0.5	0.5	0.4	0.2
180 minutes	0.3	0.9	0.8	2.2	1.0	0.5	0.2	0.5	0.7	0.6	0.5	0.4	0.2
300 minutes	0.3	1.1	0.8	2.2	1.1	0.5	0.2	0.5	0.8	0.6	0.6	0.5	0.3
Water remaining in O.P.	46	24	10	-	112	112	112	-	55	113	76	57	59
Oil Phase Composition													
Water	6	3.2	1.4	-	15.2	15.4	19	-	7.4	16.5	9.6	5.3	8
Solids	0.5	0.4	0.4	-	0.6	0.8	0.8	-	0.7	0.6	0.6	0.6	0.4
Oil	36.9	38.1	38.8	-	33.2	32.9	31.7	-	36.3	32.8	35.8	37.2	36.2
Solvent	56.6	58.3	59.4	-	51.0	50.9	48.5	-	55.6	50.1	54.0	56.9	55.4
W/O Ratio X100	16.3	8.4	3.6	-	45.8	46.8	59.9	-	20.4	50.3	26.8	14.3	22.1
S/O Ratio X100	1.4	1.0	1.0	-	1.8	2.4	2.5	-	1.9	1.8	1.7	1.6	1.1

V5-Table 2

Calibration of Apparatus in terms of Rate of Water-Wet Solids Separation as a Function of Particle Size (6 % Solid Spheres in a 1:1 Oil-Xylene Phase)

Particle Size Range, Microns	**1-30**	**13-44**	**28-53**	**53-74**	**74-105**	**105-149**
Sep^n Time Minutes	----------Separated Solids Wt% into water phase ----------------------------------					
1	-	-	-	-	95	97
2	-	81	90	91	-	-
3	78	-	-	-	-	-
4	-	-	-	-	99	99.5
6	89	95	97	97	-	-
9	-	-	-	-	-	-
15	96	98	98	98	99.5	-
30	98	-	-	-	-	-
38	-	99	-	-	-	-
Oil Loss After Sep^n	0.5	0.1	0.1	0.3	0.9	0.2

V5-Table 3

Effect of Sodium Tripolyphosphate on Other Types and Quality Beaver River Froths

Froth Composition Wt%: -	Medium:	Water - 25.	Solids - 5.	And Oil - 70.
	Bench #1:	Water - 9.	Solids - 4.	And Oil - 87.
Settled Froth Samples	Bench #1:	Water - 10.	Solids - 22.	And Oil - 68.
From Bottom of Can	Run #109:	Water - 2.	Solids - 3.	And Oil - 71.

Froth Type	**-------- Medium -------**				**-- Bench #1 --**			**Bench #1**	**Run 109**
Chemical Addition in								(Special Samples)	
Mixing - Type	-	-	-	NaP_3O_{10}	-	-	$Na_5P_3O_{10}$	$Na_5P_3O_{10}$	$Na_5P_3O_{10}$
- % on Froth	-	-	0.3	0.3	-	-	0.5	0.3	0.3
Water Phase - Type	-	$Na_5P_3O_{10}$	-	-	-	$Na_5P_3O_{10}$	-	-	-
- % on Froth	-	0.1	-	-	-	0.1	-	-	-
pH (Average) of Water Phase	7.3	9.3	9.2	9.3	6.0	9.1	8.7	8.3	9.4
Results, Wt% on Total									
Solids Removed in									
10 Minutes	40	46	50	48	8	14	20	81	82
30 Minutes	44	52	55	53	13	18	28	85	83
60 Minutes	51	55	58	56	18	25	33	88	83
120 Minutes	54	60	-	61	20	29	37	-	-
180 Minutes	56	64	-	63	22	32	40	-	-
300 Minutes	58	66	-	66	25	36	41	-	-
Solids Remaining in O.P.	23	-	22	13	33	16	27	5	9
Solids in Sludge (Diff.)	19	-	20	21	42	48	32	7	8
Oil Loss to Water in									
10 Minutes	0.9	0.7	1.1	2.7	0.1	0.2	0.4	4.6	2.2
30 Minutes	1.0	0.7	1.1	3.2	0.1	0.3	0.6	5.5	2.3
60 Minutes	1.3	0.8	1.1	3.2	0.1	0.3	0.6	5.4	2.3
120 Minutes	1.6	0.9	-	3.9	0.1	0.4	0.7	-	-
180 Minutes	1.7	0.9	-	4.1	0.2	0.4	0.7	-	-
300 Minutes	1.8	1.0	-	4.1	0.2	0.4	0.8	-	-
Water Remaining in O.P.	68	-	22	68	35	12	90	36	25
Oil Composition									
Water	8.6	-	33	10.1	1.9	1.5	47	2.2	3.2
Solids	0.7	-	0.8	0.4	0.7	0.5	0.6	0.7	0.5
Oil	36.5	-	37.3	34.8	43.2	43.5	42.0	37.2	38.6
Solvent	54.2	-	58.6	54.7	54.2	54.5	52.7	59.9	57.7
W/O Ratio X100	23.6	-	8.9	29.0	4.4	3.5	11.2	5.9	8.3
S/O Ratio X100	1.9	-	2.1	1.1	1.6	1.1	1.4	1.9	1.3

V5-Table 4

Effect of Buffer solutions in Mixing and Separation of Water-Wet Solids from Beaver River Froth - Run #109 (Froth Composition, wt %: Water -18; Solids -8; and Oil -74)

Buffer Solution	**HCl + KCl**	**HCl + KCl + Pot. Biphthalate**	**HCl + Pot. Biphthalate**	**NaOH + HCl + Pot. Biphthalate + Monopot. Phosphate**	**-**	**$Na_5P_3O_{10}$ 0.3%**	**NaOH + Borax**	**KOH + NaOH + K_2CO_3 + KBD_2**	**NaOH 1.6%**
pH - Solution	1.4	2.7	3.8	4.8	-	9.3	-	10.6	12.5
pH - Aqueous Phase	1.6	3.8	5.1	6.2	7.3	7.7	8.9	10.0	11.9
Results, Wt % on Total									
Solids removed into Water Phase									
10 minutes	61	58	54	54	54	52	53	57	51
30 minutes	62	60	55	56	56	59	60	61	51
60 minutes	63	61	56	57	56	61	61	63	51
Solids remaining in Oil Phase	14	13	14	7	11	14	12	17	12
Solids in Sludge Phase	23	26	30	36	33	26	27	20	37
Oil Loss in 10 minutes	1.2	2.0	2.0	1.7	1.5	1.6	1.3	1.9	0.4
30 minutes	1.3	2.1	2.1	1.8	1.7	1.6	1.5	2.0	0.6
60 minutes	1.3	2.1	2.3	1.9	1.7	1.7	1.7	2.0	0.8
Water remaining in Oil Phase	22	19	20	23	21	15	33	119*	230*
Oil Phase Composition									
Water	2.5	2.2	2.3	2.6	2.5	1.8	3.8	10.4	26.5
Solids	0.7	0.6	0.7	0.5	0.6	0.7	0.6	0.8	0.6
Oil	38.8	39.0	36.9	38.8	38.8	39.1	38.3	35.6	29.2
Solvent	58.0	58.3	60.0	58.1	58.1	58.5	57.3	53.3	43.7
W/O Ratio x 100	6.4	5.6	6.2	6.7	6.4	4.6	9.9	29.2	91.0
S/O Ratio x 100	1.8	1.6	1.9	1.3	1.5	1.8	1.6	2.2	2.1

* Errors in procedure.

V5-Table 5

Miscellaneous Process Effects Studied as a Function of Solids Removal from Good Quality Beaver River Froth at Standard Conditions (Froth Composition Wt % : Water -16; Solids -6; and Oil -78)

(Froth Composition Wt%: water-16, solids-6, and oil-78)

Standardized Conditions	**Yes**	**--------------------No Interface Vibration---------------------------**								**Yes**
Chemical Addition In										
Mixing - Inorganic Type	-	-	H_2O_3	$Na_4P_2O_7$	$Na_4P_2O_7$	$Na_4P_2O_7$	$Na_4P_2O_7$	$Na_5P_3O_{10}$	$CoCl_2$	$Co(OH)_2$
-% On Froth	-	-	10% of 2% Sol"	0.3	0.3	0.5	0.3	0.3	0.2	0.04
-Organic Type	AMU. Alcohol	-	-	-	Brexit 941	Brexit 7390	Brexit 2520	Brexit 2520	-	-
-% On Froth	25% In Xylene	-	-	-	0.2	0.2	0.2	0.2	-	-
Water-Type	-	Dispersed	H_2O_2	-	-	-	-	-	$CoCl_2$	$Co(OH)_2$
-% On Froth	-	Air	2% Sol^n	-	-	-	-	-	1% Sol^n	Sat. Sol^n
pH (Average) on Water P.	8.6	6.6	2.7	9.4	9.6	9.6	9.3	9.5	6.9	11.8
Results, Wt % on Total										
Solids Removed in										
10 Minutes	24	8	11	36	39	25	32	41	42	22
30 "	27	11	15	36	42	35	-	61	44	22
60 "	27	13	18	36	43	36	36	61	46	22
120 "	28	15	20	36	43	36	37	61	47	22
180 "	28	17	23	36	43	36	38	61	49	22
300 "	29	20	26	36	43	36	39	61	51	22
Solids Remaining in O.P.	17	-	-	19	14	17	6	13	18	24
Solids in Sludge (Diff.)	34	-	-	45	43	47	53	24	31	54
Oil Loss With Solids In										
10 Minutes	0.6	0.6	0.0	0.7	1.3	1.0	1.0	1.2	0.8	0.6
30 "	0.7	0.6	0.0	0.7	1.4	1.5	-	2.3	1.1	0.7
60 "	0.8	0.6	0.0	0.7	1.4	1.6	1.1	2.3	1.2	0.8
120 "	0.9	0.6	0.0	0.8	1.4	1.6	1.1	2.3	1.2	0.9
180 "	0.9	0.6	0.0	0.8	1.4	1.6	1.1	2.3	1.3	0.9
300 "	0.9	0.6	0.0	0.8	1.4	1.6	1.2	2.3	1.4	1.0
Water Remaining in O.P.	105	-	-	8	10	6	3	196	57	48
Oil Phase Composition										
Water	9.5	-	-	0.7	0.9	0.5	0.3	17.3	4.9	4.4
Solids	0.6	-	-	0.7	0.5	0.6	0.2	0.4	0.6	0.8
Oil	37.3	-	-	41.0	41.0	40.9	41.3	34.3	39.2	39.4
Solvent	52.6	-	-	37.6	57.6	58.0	58.2	48.0	33.3	33.4
W/O Ratio X100	23.5	-	-	1.7	2.2	1.2	0.7	50.4	12.4	11.2
W/O Ratio X100	1.6	-	-	1.7	1.3	1.5	0.5	1.2	1.5	2.0

V5-Table 6

Effect of Mixing on Water-Wet Solids Removal from Beaver River Froth-Run #109 "Standardized Conditions Were Not Optimum" (Froth Composition Wt %: Water -18; Solids -8; and Oil -74)

Separation Conditions	Standardized	-Experimental-					
Mixer-Type	Spatula	6 Paddle D.C. Stirrer					
(RPM)	60	60	270	670	1700	270	1000
Time in Minutes	7	15					
Chemical - Type	-	-	-	-	-	NaTPP	
- % on Froth	-	-	-	-	-	0.5	
Results, Wt % on Total							
Solids Removed into Water Phase							
10 Minutes	55	63	71	70	76	76	70
30 Minutes	57	64	73	71	77	78	71
Solids Remaining in Oil Phase	14	15	14	12	15	15	15
Solids in Sludge Phase	29	21	13	17	9	7	14
Oil Loss in							
10 Minutes	2.6	2.4	2.3	2.1	2.7	2.0	1.8
30 Minutes	2.6	2.4	2.4	2.2	2.7	2.1	1.9
Water Remaining in Oil Phase	21	12	23	10	23	6	27
Oil Phase Composition							
Water	2.0	1.4	2.4	1.1	2.4	0.7	3.1
Solids	0.7	0.7	0.6	0.6	0.7	0.7	0.6
Oil	39.5	39.5	39.3	39.8	39.2	39.9	38.9
Solvent	57.8	58.4	57.7	58.5	57.7	58.7	57.4
W/O Ratio X100	5.1	3.9	6.1	2.8	6.1	1.8	8.0
S/O Ratio X100	1.8	1.8	1.5	1.5	1.8	1.8	1.5

V6

EXPERIMENTAL TECHNIQUES AND EQUIPMENT

1. Tar Sand Sample Preparation and Storage

(a) Preparation

It is singularly important in the discussion of data related to tar sands to recognize that the variations in composition and quality are probably the major problems in producing consistent data. The variability of the tar sand feed is a constant problem especially when working on a small scale.in order to obtain a reproducible feed sample for laboratory studies, the following technique was devised and has proved to be successful.

First, a large representative tar sand sample from a given area, core, or auger hole, was obtained from the tar sand formation. If possible, it was sealed in a plastic bag after N_2 blanketing and convexed in a can. This sample was then homogenized prior to use. The homogenized step was carried out by spreading a large batch of about 50 to 100 pounds of tar sands on a clean stainless steel bench. The sample is then carefully broken down with a large spatula to aggregates of less than 1/2". The total quantity was then thoroughly mixed and returned to a nitrogen filled polyethylene bag in a metal container. Portions of 5 pounds are taken when required and screened through a 1/4" sieve, mixed, and smaller quantities of this homogenized sample are used for experiments.

Processability tests on a sample taken from an undisturbed block of tar sands and a homogenized small portion of the same sample using this technique gave the same results. Even homogenizing some friable tar sands such as Area D by grinding in a mill gave homogeneous samples and satisfactory processability results as shown by the following example.

EFFECT OF GRINDING AN AREA D (Hole 9) TAR SAND

Treatment	Undisturbed	Ground (1)
Froth Composition, wt %		
Water	40.7	39.7
Solids	5.4	5.8
Oil	53.9	54.5
Oil Recovery, wt %, in		
Froth	63.1	64.4
Water Phase	35.3	33.4
Sand	1.6	2.2

(1) Using an automatic grinding mill with 4" plates discharging material about 1/32" in size.

However, the same treatment with an Area B type tar sand resulted in the dry separation of clean sand and agglomeration of oil particles. It was preferred when working with this type of tar sand to carefully break the structure down with a spatula to about 1/4" lumps and after mixing use the sample directly. Sand separation was kept to a minimum by chopping this type of oil sand and the original sample is distributed as little as possible. The general treatment of dividing and blending large batches and then 1/4" screening of small samples have been used in all the studies reported unless otherwise indicated.

(b) Storage

Tar sand samples taken from the formation lose water from the structure. This is readily measured on many types of tar sands as a loss in weight on exposure in time. The loss in weight is of course more rapid the higher the temperature. The loss of water is believed to be due to a three dimensional capillary system throughout the structure, resulting from contact of sand grains having surface films of water. Even when tar sands are kept in air-tight polyethylene bags at room temperature, condensation of water occurs on the inside surface. The tendency to lose water appears to be less at low temperatures of about 40°F. Hence, samples as a rule were stored at about this temperature.

Freezing tar sand samples is not recommended as it affects the capillary water films. Based on a brief beaker hot water separation study, processability was observed to deteriorate with the number of freezing cycles.

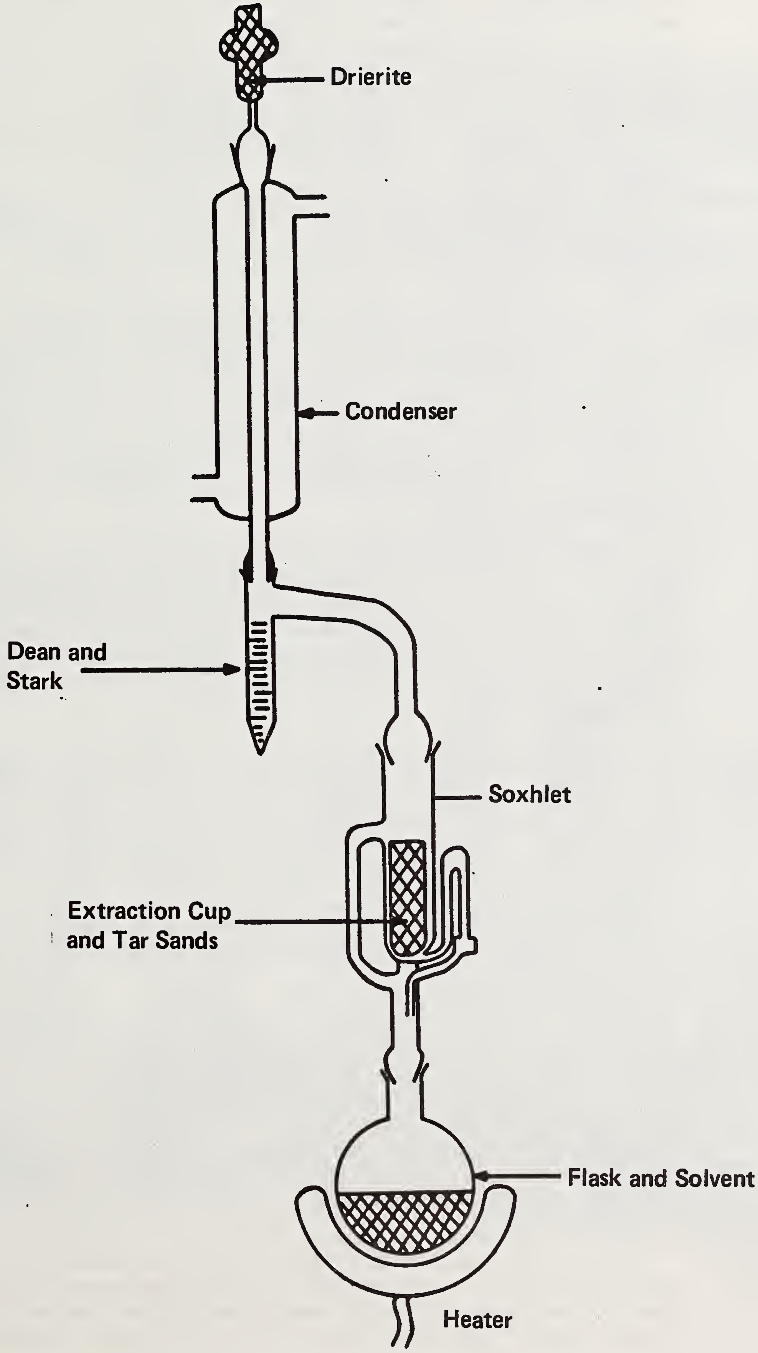
2. Tar Sand Composition

The technique combined the features of a Dean and Stark water determination and a Soxhlet extraction as shown in Figure 1. Specifically, a weighed 100 gram sample of tar sands was introduced into a dry 33 by 80 milli meter Soxlet extraction cup and the oil is extracted with either toluene or benzene. The water is collected overhead in the Dean and Stark side-arm. The solids remain in the extraction cup.

A few refinements to this simple technique are used to obtain more accurate analyses. First, the condenser is washed down with toluene to obtain what is referred to as a normal wettage for the Variac setting used in the air-conditioned laboratory. This normal wettage has been measured to be 0.1 cc by removing the water in alcohol and obtaining a Karl Fisher analyses. Correction is also made for the water solvent meniscus in the side-arm. These two corrections give more accurate values for water. Second, some clay passes through with the solvent and oil, particularly if surging is encountered in the early stages of extraction. The solvent-oil mixture is centrifuged at 2000 rpm for an hour and the solvent oil mixture is decanted. The clay is washed free of oil by mixing with solvent and centrifuged again, dried and weighed. In most operations the fines are about 0.1 gm. The solids are removed, dried and weighed to which the centrifuged solids from the extracted solvent-oil phase are added. This tedious operation was avoided by using a heavier wall extraction cup. Also, in order to carry out a reasonable number of experiments more quick-

V6-Figure 1

Apparatus for Determining the Composition of Mixtures of Solids-Oil-Water



ly, the oil was obtained by difference. This was checked to be satisfactory by removing the solvent by vacuum distillation. Thus, it became important to only measure water, and solids accurately. The standard error for oil determination was ± 3% on oil content.

In addition to determining the toluene or benzene soluble oil, water and total solids, the solids are sometimes re-extracted with polar solvents such as acetone or pyridine, to determine residual polar compounds of the oil not soluble in the aromatic solvent and associated with the solids; e.g. , see tar sand characterization studies. Evaporation of the solvent on a water bath in a fume hood yields the weight of this residual oil as a direct percentage on tar sands.

3. Froth Composition

A similar analysis to that for tar sands procedure was carried out with froth. The froth was skimmed directly into the weighed cup, that is then extracted in the Soxhlet Apparatus (Figure 1). The same methods of measuring water, solids and oil were used. Again the oil measurement by difference was checked by distillation. In many cases a gravity was obtained which serves to check the amount of oil present; although this method is not as accurate as distillation, it is quicker.

4. Water Phase Composition

The total decantings from the separation were generally evaporated to dryness and ashed. The ash was corrected for an average fines ash of 92 wt % in the earlier studies. This was based on ash determinations on oven dried samples of separated oil-free fines 325- and other "clay" samples from different locations at Mildred Lake. The average ash value of ten of these latter samples was 92.06 wt % with a standard deviation of 0.27. This suggests that fines have an average of 8 wt % water of hydration, which is chemisorbed in the clay lattice. In more recent pot extraction studies, Soxhlet extractions were used to obtain oil-free solids for weigh balance, and other mineral studies.

The latter technique gave greater accuracy and provided more absolute oil recovery, and gave a closer agreement between calculated tar sand compositions from hot water extractions and direct composition determinations on tar sand feeds. The oil content of the water phase has also been checked by solvent extractions on water phase sludges after evaporation of the bulk of the water and measurement of oil in the amount of solvent used. This is a good method for obtaining oil and solid balances in separation, provided oil in solvent can be measured accurately by infrared spectrometry.

5. Sand Phase Composition

The wet sand phase from separation after being washed free of oil and clay particles, was dried and ashed. The ash was corrected for an average clean sand (Area B) ash of 99.66 wt % in earlier studies. More recent studies utilized ash distribution of solids to obtain more absolute oil recovery values. This latter procedure is highly recommended, as it was found with many tar sands that the ash on the clean sand varies appreciably from sample to sample due to its' clay mineral content. Nevertheless, as the earlier studies were a series carried out to investigate a specific effect with a specific tar sand, the comparative information obtained is still valid. Soxhlet extraction, Figure 1, is also recommended, provided oil in solvent can be measured accurately by infrared analysis.

6. Solids Distribution

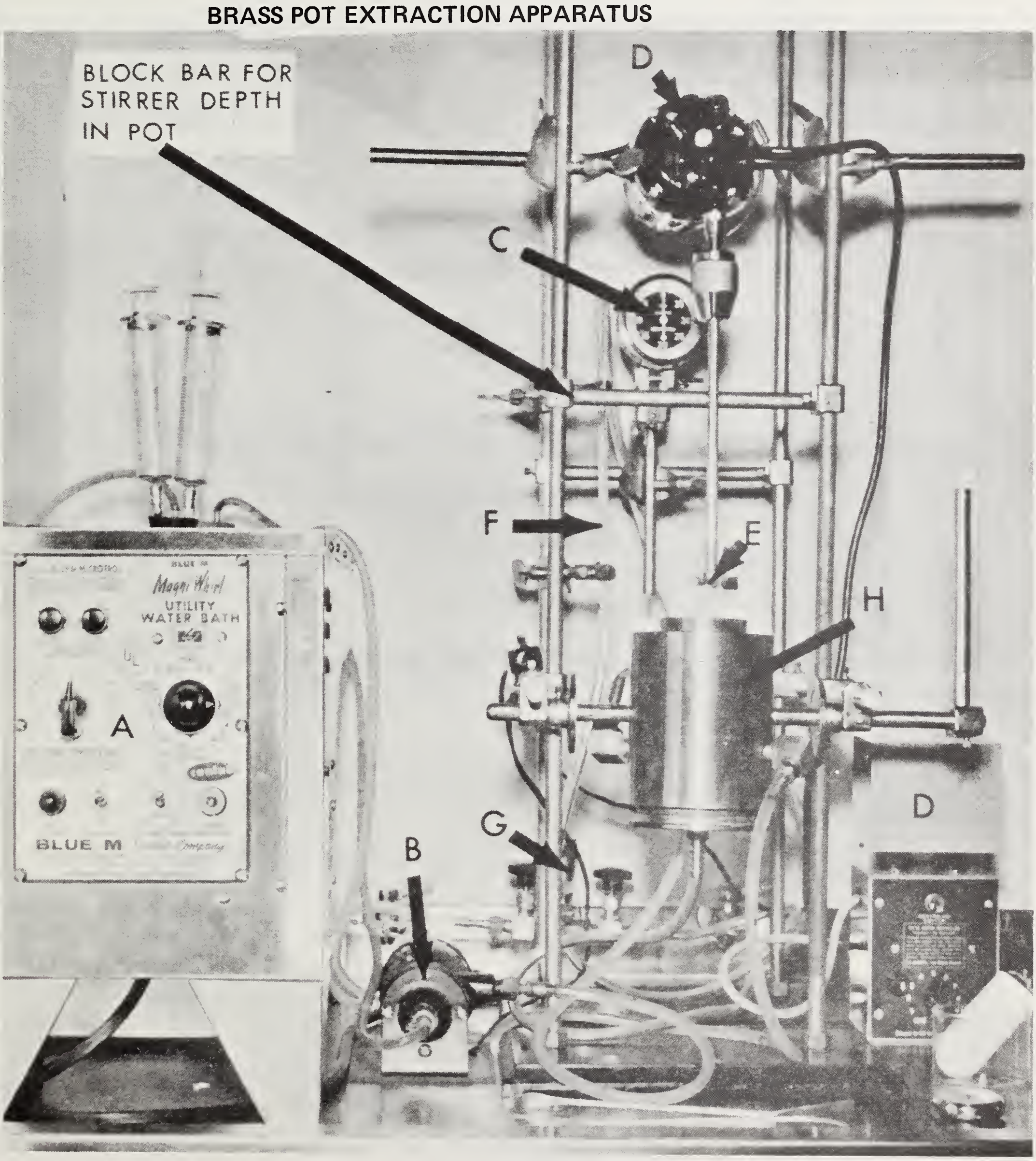
The total extracted solids from Soxhlet extraction of the tar sands are finally washed with acetone, pyridine, acetone, water and dried. The solids are then re-dispersed by gently mixing in the mortar with a pestle with water containing small quantities of sodium silicate, 0.1% solution, as a clay dispersant. The solids are then wet screened through a series of 3" sieves. The quantities recovered on each sieve are dried, weighed, and ashed. Weight balances average 99.2 wt % and calculated total ash from the individual ashes agree very closely with those obtained on a total solids sample.

7. Pot Method of Flotation

This technique was developed to give better process variable control than was achieved in earlier beaker studies. A major problem in any small scale separation is transference of heat and control of temperature. A cylindrical brass pot was designed to achieve this end, Figure 2. A hot water circulation system was built into the wall. The hot water was pumped from a constant hot

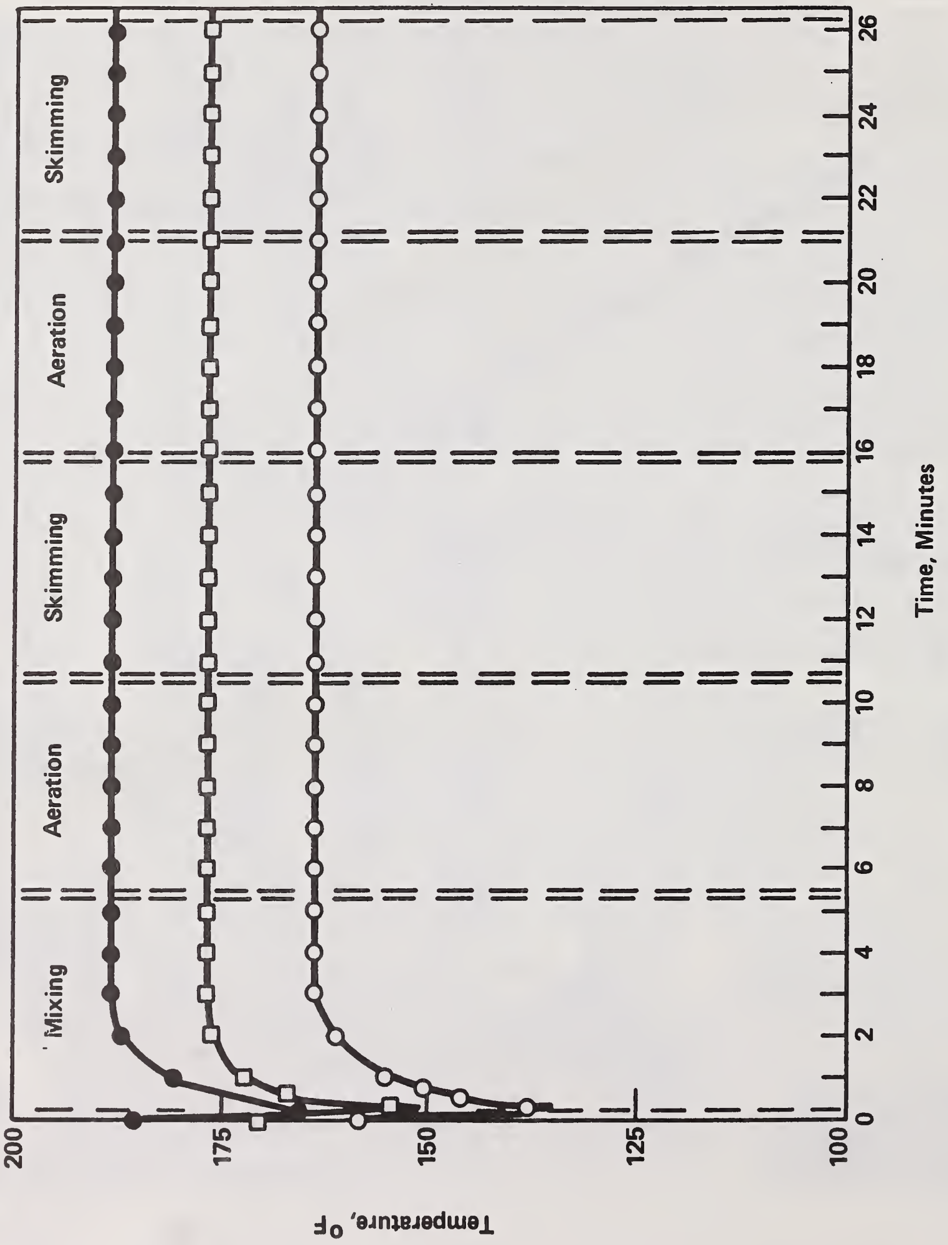
V6-Figure 2

Brass Pot Extraction Apparatus


BRASS POT EXTRACTION APPARATUS
BLOCK BAR FOR STIRRER DEPTH IN POT
D
C
F
E
H
Magni Whirl
UTILITY WATER BATH
A
BLUE M
B
G
D

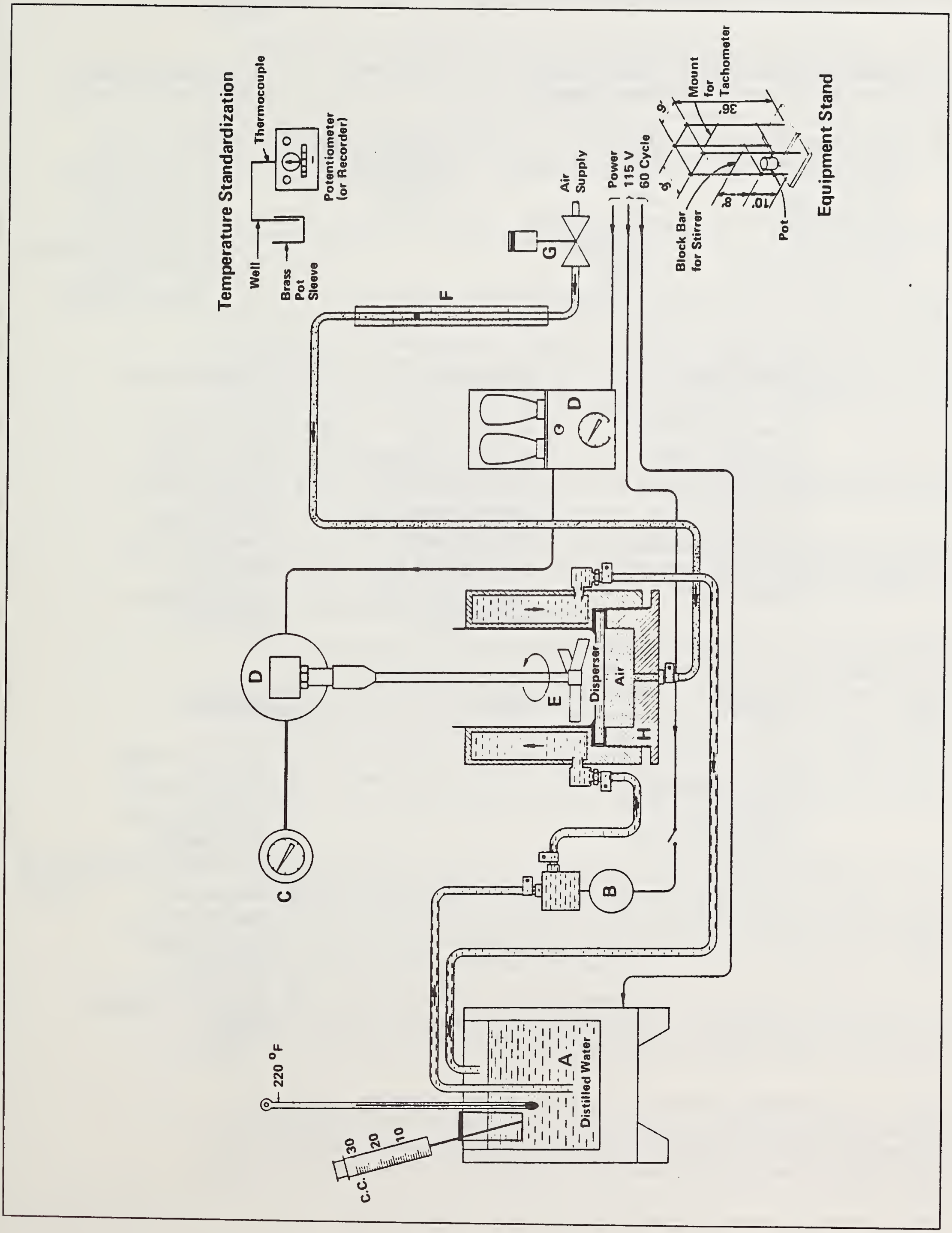
V6-Figure 3

Some Typical Temperature Profiles Measured with a Recorder



V6-Figure 4

Laboratory Brass Pot Tar Sand Extraction Equipment



V6-Table 1

Laboratory Tar Sand Extraction Equipment

A. Constant Temperature Water Bath	**B. Water Circulation Pump (Midget)**	**C. Tachometer**	**D. Electronic Stirrer (Constant Torque)**
Blue "M" Magniwhirl Model No. M.W. 1110 Cat. No. 84-621 Max. Watts 800 115 Volts, $251 From Fisher Scientific	Model B-1 Cat. No. 13-874-93 1/20 115 Volts, $74 From Fisher Scientific	0-4000 RPM (3 range) Metronitripletac HP Motor	#4650 complete 115 Volts, 60 Cycle $110 From Cole Palmer Instrument and Equipment Company, 7320 N. Clark St., Chicago 26, Illinois

E. Stirring Element	**F. Air Rotameter**	**G. Air Control Valve**
Three Blade 304 S/S 2" Diameter, Serial No. 1460A41. To fit 5/16" Shaft, $6 from: Greey Mixing Equipment Ltd., 100 Miranda Ave., Toronto	1. High Flow Rates Tube 02-F-1/8-20-5/21 1/8" Sapphire Ball. 2. Low Flow Rates Tube 08F-1/16-16-4/74 1/16" Stainless Steel Ball. #24 each from Fischer Porter	1/8" or 1/4" Fine Metering Valve with Small Orifice size 0.055 with Vernier #22. From either Hoke or Nuclear Products (Nuprovalve)

H.	**Brass Pot**	**I. Sleeve**	**Miscellaneous**
1. 2.	$125 Disperser, Gaskets and Fittings $25 Supplied from Sarnia		1. 3/16" Tygon Tubing 2. #12 Brass Clamps 3. 30 cc Hypodermic 4. Spoon Spatulas 5. Stop Watch 6. Thermometer 7. Stands (14670 x 2 $4 from Fisher) 8. 1/2" Rods 9. Flexoframe Connectors 666-20

water bath through the jacket and back into the bath. Typical temperature profiles for the separation are shown in Figure 3A. An inner sleeve was also employed for obtaining oil loss not collected in skimming. The sleeve was also coated with a baked oil glass film in experiments with additives.

The filter bottom to the pot was used to give good air dispersion and high aeration volume. The filter was originally made of porous glass, but due to a high breakage rate under thermal stress, sintered stainless steel of porosity H was used, Figure 4. The intensity of mixing in the separation is also critical, so a high torque DC stirrer was employed to give constant low RPM's in mixing the paste-like tar sand slurry with water. The RPM's of the stirrer were measured by a tachometer and was controlled electrically to give a donut shaped homogeneous slurry in the pot without override of oil sands.

Air addition was measured by a calibrated rotameter using a fine control valve to give reproducible settings at any desired air rate. The apparatus is shown in Figures 4 and equipment details in Table 1.

This simple system achieved much more precise control than was obtained in the earlier beaker studies and provides accurate and reproducible changes of process conditions. However, the separation of the system into three phases; i.e. , froth water and sand phase was essentially the same technique as used in the beaker extractions. The froth was manually skimmed, and the water phase and sand decanted separately. No small scale mechanical skimming has yet been developed which can be substituted for the manual technique used. Development of this technique needs practice.

The procedure for separating tar sands using this pot extraction apparatus is outlined in Table 2. A general weight balance calculation shown in Table 3, was varied depending on the type of analytical procedures used, as discussed above.

An example of the reproducibility that can be obtained using this technique is shown in Table 4. In this example, the repeatability of extraction results at three different temperatures with an Area D tar sands is shown. The tar sand was a spot sample of homogenized bench unit feed (July 1962) obtained from west of Hole 9.

It will be noted that the standard deviations are small, indicating that good reproducibility can be achieved. It is surprising that, in spite of the manual skimming employed, a high reproducibility in the water content of the froth is obtained. The tar sand composition calculated from the analysis of the three streams obtained for each experiment is shown. These results show a close agreement with the feed analysis that had a much higher standard error in determination. Thus, the pot technique measures the property of floatability of the bitumen that appears to be achieved more accurately. These data give a good indication of the reliability of the extraction results, which is a very useful research tool for the evaluation of process variable in hot water flotation.

8.pH Measurements

pH measurement were originally carried out using a Fisher titrimeter (Catalogue #9-311A), which was subject to fluctuations. The accuracy of earlier pH work is subject to question. More recent measurements in the brass pot separation studies have been made with a new Beckman pH Zermatic Model 76 meter with temperature compensation and an expanded scale range for accurate measurements of 0.01 within any 2 pH range.

Great care of the glass and calomel electrodes must be taken when using oil and clay suspensions frequently in the presence of inorganic salts. A high degree of cleanliness and regeneration was maintained at all times, and calibration was a daily routine with buffer solutions.

This laboratory technique was used successfully for measuring processability of tar sands. As a research tool, it has been used to study most of the process variables. However, variations in tar sand feed quality are probably the most significant variable contributing to differences in results of separations. Some of the findings are listed below to demonstrate the effectiveness of the tests.

V6-Table 2

A Modified Pot Extraction Procedure for Laboratory Tar Sand Separations

1. Switch on distilled water bath and bring temperature up to about 183°F for standard operation temperature of 180°F in the pot.
2. Turn on water circulation pump, D.C. stirrer control, and the air pressure on the bottom of the filter.
3. Control water bath to obtain a constant operating temperature of 180°F in the pot.
4. Transfer 30 cc water or solution from beaker suspended in bath to brass pot with hypodermic syringe.
5. Lower stirrer into pot, turn on and set revolutions at 800 rpm.
6. Add 100 g of freshly weighed, well homogenized tar sands to water in pot.
7. Start stop watch and stir for 5 minutes.
8. Flood mixture with 70 cc water at bath temperature.
9. Stir for 5 minutes with no aeration.
10. Skim bulk of froth for 2-1/2 minutes.
11. Stop stirrer, skim remaining froth for 2-1/2 minutes.
12. Start stirrer and turn on air. Set air rate at (1) cubic feet per hour for 5 minutes equivalent to 0.38 cu ft/lb tar sands.
13. Repeat steps 10 and 11.
14. Repeat 12 at max(1) cubic feet per hour, and then steps 10 and 11.
15. Recover the froths separately in soxhlet cups, and analyze immediately for water, solids, and oil contents.
16. Add 30 cc water and mix for 1 minute. Raise stirrer with movement suitable to wash off any adhering sand. Allow to settle 1/2 minute, tip pot to decant water phase into a weighed container.
17. Measure pH of water phase; and zeta potential of a drop in distilled water.
18. Centrifuge the water phase. Measure pH, specific conductance, and zeta potential of an original drop of water phase in the centrifuged-clear mother liquid, which requires acidification at high pH.
19. Dry centrifuge tube and analyze for solids and oil contents.
20. Lower stirrer and repeat step 16 twice, collecting washings.
21. Raise stirrer and wash with 15 cc water. Raise sleeve and wash off sand. Remove sleeve free of adhering sand.
22. Decant sand and wash pot free of sand with water into a weighed container. After settling decant excess water into washings container. Dehydrate and measure solids and oil content of both separation sand and water washing phases.
23. Oven dry sleeve, stirrer and spatulas to obtain a dry froth loss assumed to have the same ratio of oil to solids as in the third measured froth.
24. Enter data into transmittal forms for calculation of results.
25. Tabulate results with measurements of pH, zeta potential conductance salt amount and types.

* Scaled up equipment and procedure can give similar results and provide quantities of product streams for further evaluation.

(1) Maximum amount is less than 0.38 cu ft/lb tar sand to avoid frothing over with high-clay oil sand samples.

V6-Table 2a

A Modified Pot Extraction Procedure for Laboratory Tar Sand Separations

1. Maintain high level in bath with distilled water. In the initial setting up of equipment, flush brass pot's internal heating system to remove any thread goop. Keep water system clean at all times. Use clean distilled water or solution from beaker suspended in water bath for all operations.
2. Before daily experimentation, pressure test hot for air leaks and check air dispersion. Seals may leak in initial warm up, while bottom plug is being heated.
3. Keep an air pressure on the bottom of the disperser during all operations, to avoid loss of water through filter.
4. In the transfer of water from the beaker suspended in the bath to the operations, first fill and discharge the hypodermic three times to preheat. If solutions are to be used, keep in closed system suspended in water bath.
5. In mixing, check that the tar sands goes immediately into slurry and there is no hang up on walls of the pot. Immediate washing down with 5 cc water aliquots is used in these cases to obtain homogeneous slurry and avoid time loss. Although it is seldom required, certain marginal quality tar sands require more water in mixing than the suggested standard.
6. Sleeve with thermocouple insert is used to check temperature of operation using a potentiometer or recorder.
7. When flooding, add water down side of pot. In setting air rate turn valve so that ball passes setting then reduce flow. This clears filter and gives good subsequent air dispersion.
8. To clean filter when required, remove from pot and wash mainly the surface with toluene followed by acetone and water. More drastic treatment such as hot alkali and acid is only required very infrequently.
9. Skimming froth is a most important part of the procedure. Only practice can result in consistent froth qualities from operations on a given tar sand. The technique used requires first a "scoop" action to remove the bulk of the froth in small amounts leaving a thin layer of froth on the surface. Care must be taken not to disturb the froth-water interface and push froth back into the water phase. When most of the bulk froth has been removed after about 2-1/2 minutes skimming, the stirrer is then turned off. Stirring is used in the intial skimming operation to disengage any oil particles which were mixed in the sand phase during internal agitation from aeration and to help maintain oil particles in suspension in the water phase. The remainder of the froth is gently drawn to and up the side of the pot sleeve until a clean water surface is obtained. A clean up of the sleeve walls and stirrer shaft for any small quantities of froth is then carried out. Operations with poor quality tar sands such as Area D sometimes results in a few oil particles suspended in the water phase just below the clear water surface. No effort is made to recover these oil particles as froth.
10. When using gases other than air, rotameter calibration is carried out to ensure equivalent volumes of flotation gas in comparative experiments.

V6-Table 3

Data Summary and Weight Balance Calculations (100 g Tar Sand Charge)

(Note: Output data is more consistent and relative. Input data probably reflects errors in tar sand analyses)

Calculation(3)	Weight in Grams	Percent
Composition of Froth (Wet Basis)		
Water collected in Dean and Stark (Corrected)	a	100 a/c
Solids (dried) in Extraction cup + Centrifuged solids	b	100 b/c
Oil (by difference)	c - a - b	100(c-a - b)/c
Froth skimmed in separation	c	100
Total Froth (Wet Basis)		
Froth skimmed in separation	c	
Froth "loss" to beakers and spatulas (dry = x)	$d = \frac{xc}{c-a}$	
Total Froth	c + d	
Yields of Three Phases (Water Free Basis)		
Froth	$\alpha = \frac{(c+d)(c-a)}{c}$	$100\,\alpha/(\alpha + e + f)$
Sludge	e	100 e/(a + e + f)
Sand	f	$100\,f/(\alpha + e + f)$
Total oil and solids	$\alpha + e + f$	100
Material Recovery (Water Free Basis - Input)		
Water Content of Tar Sand	g	g
Oil and Solids in tar sand	100 - g	100 - g
Material Recovery	$\alpha + e + f$	$100\,(\alpha + e + f)/(100 - g)$
Oil Recovery and Balance (output)		
Oil in Froth	$\beta = \frac{(c-a-b)(c+d)}{c}$	$100\,\beta/\ \beta + (eh) + (fi)$
Oil in Sludge	eh(1)	$100\,eh/\beta + (eh) + (fi)$
Oil in sand	fi(2)	$100\,fi/\beta + (eh) + (fi)$
Total Oil	$\beta + (eh) + (fi)$	100
Oil in tar sand (input)	j	j
Oil in froth	-	$\beta/j \times 100$
Tar Sand Composition (Output)		
Oil	$k = \beta + (eh) + (fi)$	
Water	$l = 100 - (\alpha + e + f)$	
Fines	$m = b + e(1 - h)$	
Sand	$n = f\,(1 - i)$	

(1) h = 1 - (ash on sludge/ash on oil free fines) or oil %/100 from soxhlet extraction.

(2) i = 1 - (ash on sand/ash on oil free sand) or oil %/100 from soxhlet extraction.

(3) A water balance can also be readily calculated in a similar way, although some water loss occurs through vapourization.

V6-Table 4

Reproducibility and Temperature Studies (Brass Pot) with a Sample (#1) of Homogenized Bench Unit Tar Sands Feed

Tar Sands from Area D, west of Hole 9 was homogenized by C.S.A. for July Bench Unit Operations. A spot sample (#1) was taken from a portion of this large batch was used in these experiments.(1) The Brass Pot Standard Procedure at three different temperatures was used.

Temperature, °F	150						170						190					
Experiment No. D-32	1	2	3	4	Avg.	Std.Dev.	5	6	7	8	Avg.	Std.Dev.	9	10	11	12	Avg.	Std.Dev.
Froth Composition, Wt %																		
Water	45.2	42.7	43.1	43.2	43.53	1.12	47.0	45.5	43.8	45.8	45.56	1.33	45.4	46.4	43.6	45.9	45.35	1.20
Solids	25.1	25.3	26.0	24.2	25.16	0.77	21.6	23.1	24.1	22.2	22.75	1.10	19.8	21.8	24.7	19.4	21.27	2.57
Oil	29.7	32.0	30.9	32.6	31.32	1.29	31.4	31.4	32.1	32.0	31.70	0.39	34.8	31.8	31.7	34.7	33.23	1.76
Wet Froth, Wt %(2) from																		
First Aeration	83.3	77.3	80.8	85.4	81.91	2.80	78.5	75.4	79.5	84.4	79.46	3.71	60.9	69.5	57.5	68.1	63.98	5.76
Second Aeration	16.7	22.7	19.2	14.6	17.92	2.80	21.5	24.6	20.5	15.6	20.54	3.71	39.1	30.5	42.5	31.9	36.02	5.76
Yields, Wt % (water free basis)																		
Froth	16.3	17.1	17.1	16.8	16.84	0.39	15.4	16.4	16.7	16.1	16.14	0.59	14.7	15.5	15.9	15.3	15.33	0.50
Water Phase	4.8	4.2	4.4	4.2	4.40	0.31	5.0	4.5	4.3	4.3	4.54	0.31	5.0	4.8	4.9	4.9	4.91	0.07
Sand	78.9	78.7	78.5	79.8	78.76	0.25	79.6	79.1	79.0	79.6	79.33	0.36	80.3	79.7	79.2	79.8	79.76	0.46
Oil Recovery, Wt % in (output)(3)																		
Froth	92.8	93.3	93.3	94.3	93.42	0.60	93.5	93.9	94.1	94.4	93.96	0.40	91.1	94.0	91.3	93.2	92.45	1.44
Water Phase	4.7	3.8	4.5	3.7	4.17	0.49	4.1	4.3	4.2	4.0	4.15	0.16	6.8	4.2	6.3	4.7	5.47	1.25
Sand	2.5	2.9	2.2	2.0	2.40	0.40	2.4	1.8	1.7	1.6	1.90	0.38	2.1	1.8	2.4	2.1	2.08	0.23
Tar Sand Composition Wt % (cal^c)																		
Oil(4)	9.1	9.9	9.6	9.9	9.66	0.37	9.4	9.8	9.8	9.7	9.68	0.21	10.0	9.4	9.5	9.6	9.62	0.27
Water(5)	4.0	3.2	3.4	3.0	3.39	0.42	3.5	3.0	2.9	3.4	3.21	0.29	2.7	3.2	3.3	2.3	2.89	0.46
Fines(6)	11.4	11.0	11.4	10.6	11.10	0.38	10.5	10.7	10.7	10.2	10.52	0.27	9.4	10.4	10.9	10.2	10.19	0.64
Sand	75.5	75.9	75.6	76.5	75.86	0.42	76.6	76.5	76.6	76.7	76.60	0.12	77.9	77.0	76.4	77.9	77.30	0.77

(1) The 5 lb spot sample (#1) used in these experiments was analysed by Soxhlet Extraction and sieving; and by oven drying and ashing and found to contain 9.6% oil, 3.3% water, 5.8% 325-fines and 81.3% sand.

(2) Wt % on total froth.

(3) Essentially the same as in pot, see note 1.

(4) Grams of oil recovered, Wt %.

(5) 100- (grams of oil and solids recovered).

(6) Solids recovered in froth and water phase.

Froth quality and oil recoveries are not significantly affected by changes of water in mixing over a wide range. Lowering the water below about 15% in slurrying results in poor separation with no improvement in oil recovery using gently mixing. This is contrary to the findings of Dr. K. A. Clark working with Bitumount tar sand. Increasing mixing intensity and to a lesser extent mixing time, increased the water and solid content of the froth and also the oil recovery. Mixing tar sand with cold water for extended periods of time appears to have no detrimental effect and perhaps slight beneficial effects on subsequent separation. Hence hydraulic transportation of tar sands should not be harmful to separation.

Multiple staged skimming can achieve very high oil recoveries from tar sands. The approach was subsequently adopted by CSA in their bench unit. For the same equivalent total air volume, higher air rates for short periods are more effective for attaining high recoveries of good quality froth than low air rates for longer times. Oil recoveries have been found to increase linearly with the log of the air rate used in pot lab extractions. High air rates, in general, result in a high solid content (or solids/oil ratio) in the froth.

The above observations indicate that both oil recovery and froth quality can be optimized by separating the oil from the tar sands in a number of cells arranged in series. Very gentle agitation with little or no aeration should be used in the first cell, with increasingly severe conditions in successive cells. Stripping the separated sand phase with air is beneficial for gool oil recovery.

Essentially no effect of temperature on oil recovery in the range of 120-190°F has been found with a number of good and poorer quality tar sand provided aeration is used. Higher temperature operations appear to give slightly less solids in the froth but water content tends to increase, i.e. , emulsification of oil and water can be reduced directionally by operating at lower temperatures. This is supported by interfacial tension data. The small effect of temperature suggests that it may be possible to operate large scale plants at lower temperatures of 130-150°F than the conventional 180°F, just as successfully. This is particularly true if froth can be upgraded in subsequent process operations. The same temperature effect was subsequently demonstrated in Bench Unit studies.

Oil recovery is a function of the "naturally occurring pH" of the tar sand.

(i) Neutral to alkaline tar sands give high oil recoveries and good froth quality.

(ii) Neutral to acidic tar sands give low oil recoveries and poor oil froth quality.

Froth quality correlates with fines (325-) content of the tar sands, and hence the concentration of fines in the water phase. Oil content of tar sand together with fines content and pH have been found to be the three primary correlating variables with processability. Development of a more refined correlation may enable the prediction of separation results from tar sand inspection data. Laboratory extraction data on oil recovery correlates generally with results obtained in the bench unit on similar tar sands. Laboratory extraction data on froth quality shows the same general pattern as results obtained in the bench unit on similar tar sands. Laboratory extraction data on froth quality shows the same general pattern as results obtained in the bench unit correlated on the basis of oil content of tar sands. The froth from the bench unit contains significantly more water and very slightly less solids on a percentage basis. This may result from either higher mixing intensity or relatively longer mixing times in the Bench Unit.

In general, blends of different tar sands show processability proportional to the amounts and behavior of the individual tar sands. There did not appear to be any synergistic or antagonistic effects from blending. Augering did not affect processability significantly. Successive freezing and thawing result in decreased tendency of the oil to float, although clean sand will separate. This suggest that the processability of tar sands above the frost line will deteriorate over the years.

Separations in the pH range of 8-10 result in high oil recovery in the froth, which has low water and solids content. This pH condition also corresponds to maxima for:(a) dispersion of particles in suspension (highest negative charge or zeta potential), (b) polyvalent ions precipitation, (c) dissociation of surfactant carboxylic acid groups (highest negative charge on oil particles) and minima for:(a) contact angle or highest hydration of solid surfaces, (b) amount of sodium salt added (notably phosphates and also silicates).

The more critical process variables for better physical separations are:

- *(a) low mixing intensities to effect break down of the tar sand structure in water, and*
- *(b) staged separation in a series of flotation cells with little or no air addition in the first, and increasing amounts of air, and increasing mixing intensities in subsequent cells.*

9. Zeta Potentials

A Zeta-Meter was used to measure the zeta potentials on oil and solid particles, Figure 5.The suspensions were viewed with a sterioscopic microscope with bounced-beam illumination. The electrophoresis cell was made of select grade plexiglas that was used with concentrations without thermal overturns. The cell was resistant to sulphuric, nitric, hydrochloric, and other acids, as well as, to sodium hydroxide. The Zeta-Meter had a stable power supply with both voltage and current meters. The timer was controlled by a sensitive microswitch. Platinum electrodes were used and the proper depth of focus was carefully obtained by bringing a positioning line into sharp focus. The effect of ionic strength on thickness on the diffuse layer of counterions is illustrated in Figures 6 and 7.

The average time in seconds for a particle to traverse one ocular division was obtained at a point in the circular tube of the cell where no electro-endoosmotic liquid movement occurred. This point for a cylindrical cell in a horizontal position was at a distance of 14.7% of d (diameter) from the cell wall in a horizontal mid-plane. A set of curves corresponding to various field strengths (volts per cm) and objective magnifications enables ready determinations of the electrophoretic mobility. Since EM is expressed in microns/sec per volt/cm, it involves neither the viscosity nor the dielectric constant of the medium.

The Zeta Potentials were estimated from the electrophoretic mobilities by using a conversion chart based on the Helmholtz Smoluchowski formula:

$$ZP = EM.\,4V_t/D_t \qquad \text{or} \qquad EM = ZP.\,D_t/4V_t$$

where: ZP = Zeta Potential of the particles (esu).

EM = Electrophoretic Mobility of the particles in cm/sec per esu volt/cm.

V_t = Viscosity of medium in poise at any temperature.

D_t = Dielectric constant of medium at any temperature.

With further simplifications and unit conversions, the equation for ZP becomes:

$$ZP = 113{,}000\ V_t.\,EM/D_t.$$

where: ZP = Zeta Potential in millivolts.

V_t = Viscosity of medium in poise at any temperature.

D_t = Dielectric constant of medium at any temperature.

EM = Electrophoretic mobility in microns/sec per volt/cm.

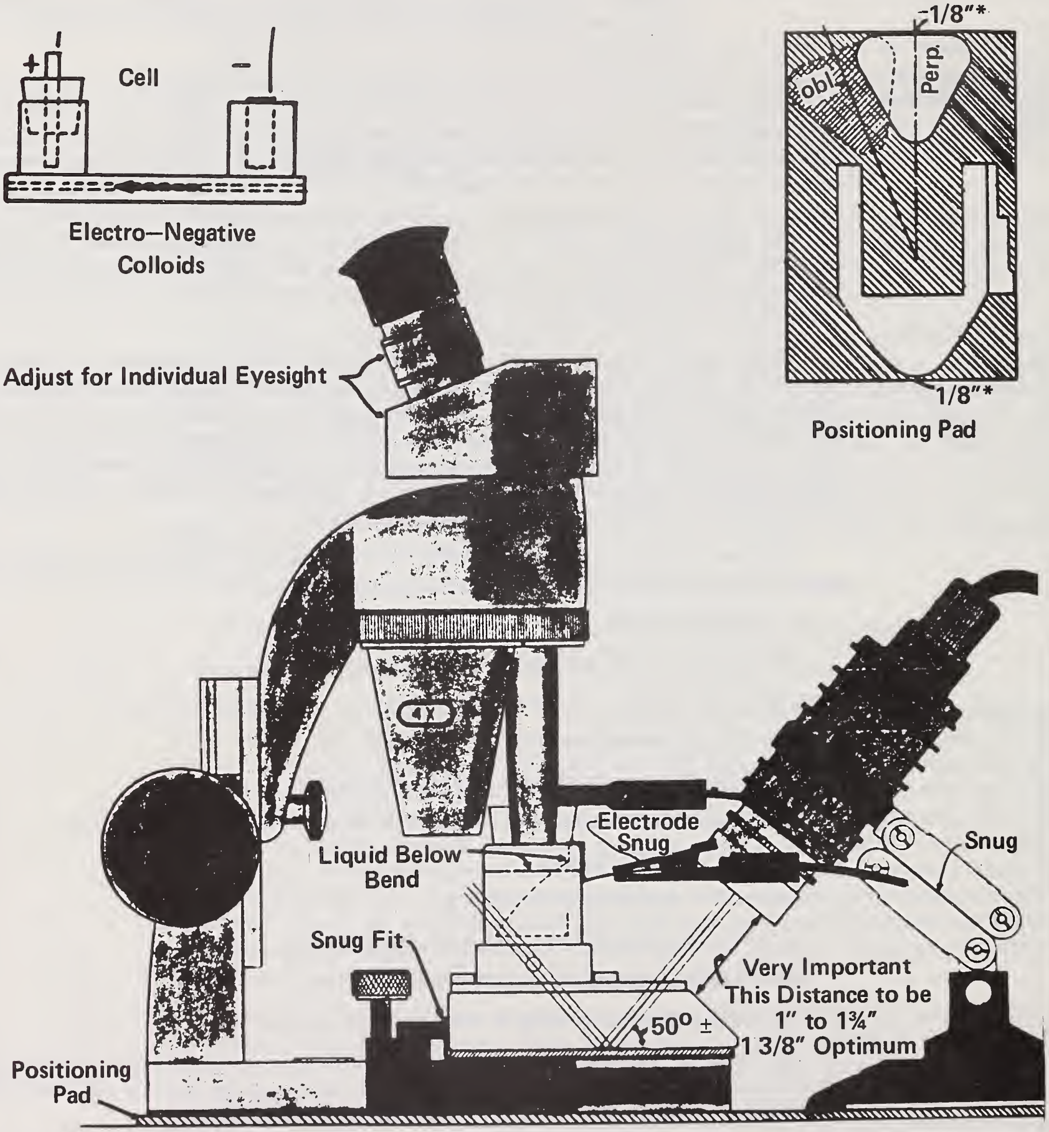
This equation can yield a curve for converting EM to ZP at any temperature by employing the corresponding values for dielectric constant and viscosity of the medium. For water at 20°C the dielectric constant is 80.36 and the viscosity in poises is 0.0100.

10. U. V. Fluorescence

A Turner Model 110 fluorometer was used to measure aqueous solutions that had been in contact with oil or tar sands. Fluorescence varies linearly with concentration in the range studied. Hence, relative fluorescent values were obtained by multiplying the fluorescence measured by the number of equal volume dilutions and by an experimental constant. This constant was found to be 0.92 ± 0.03. This instrument was very stable and sensitive and was standardized with distilled water to zero. The fluorescence of samples was measured several times

V6-Figure 5

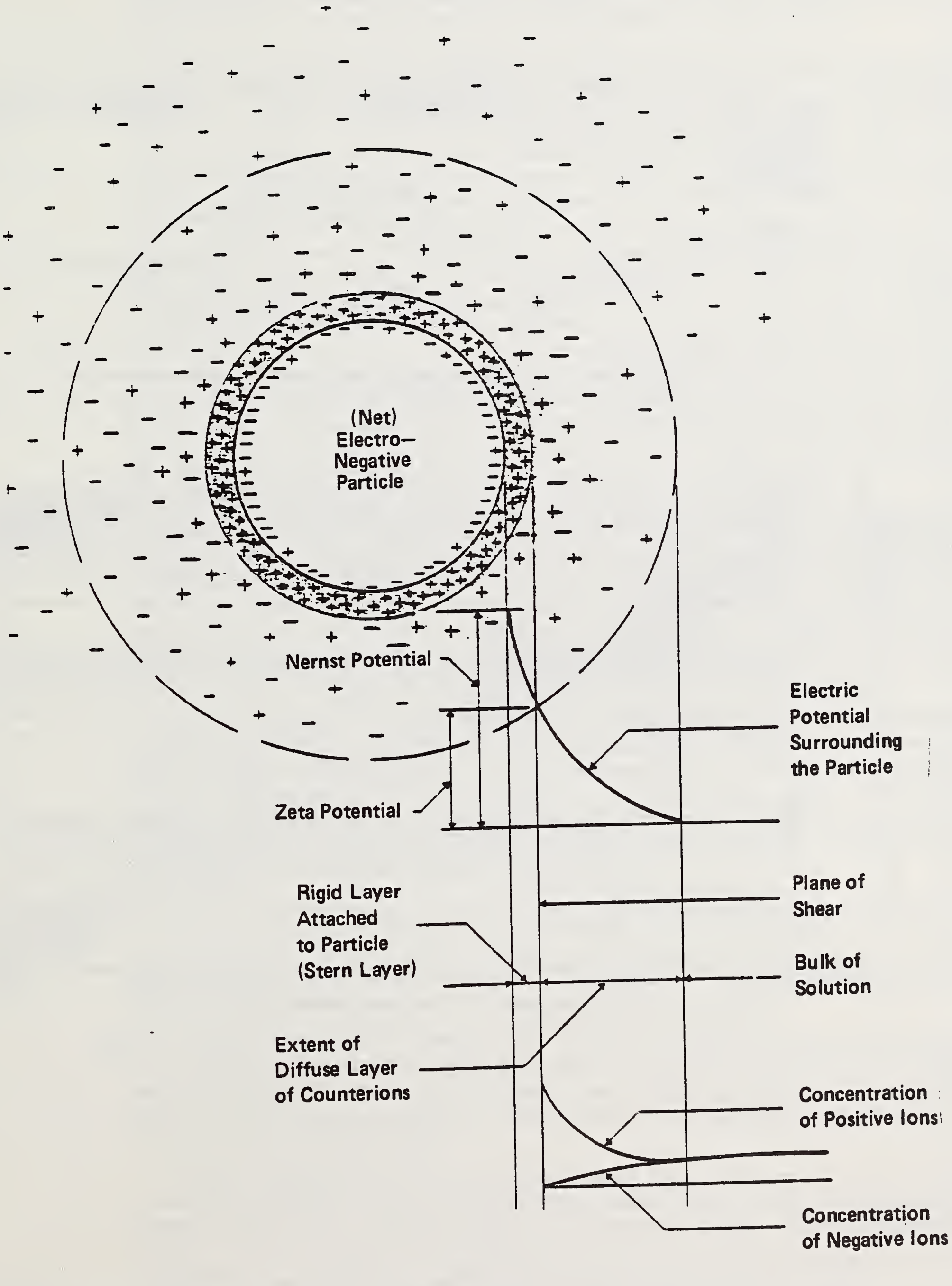
Zeta-Meter



POSITIONING OF CELL AND ILLUMINATOR

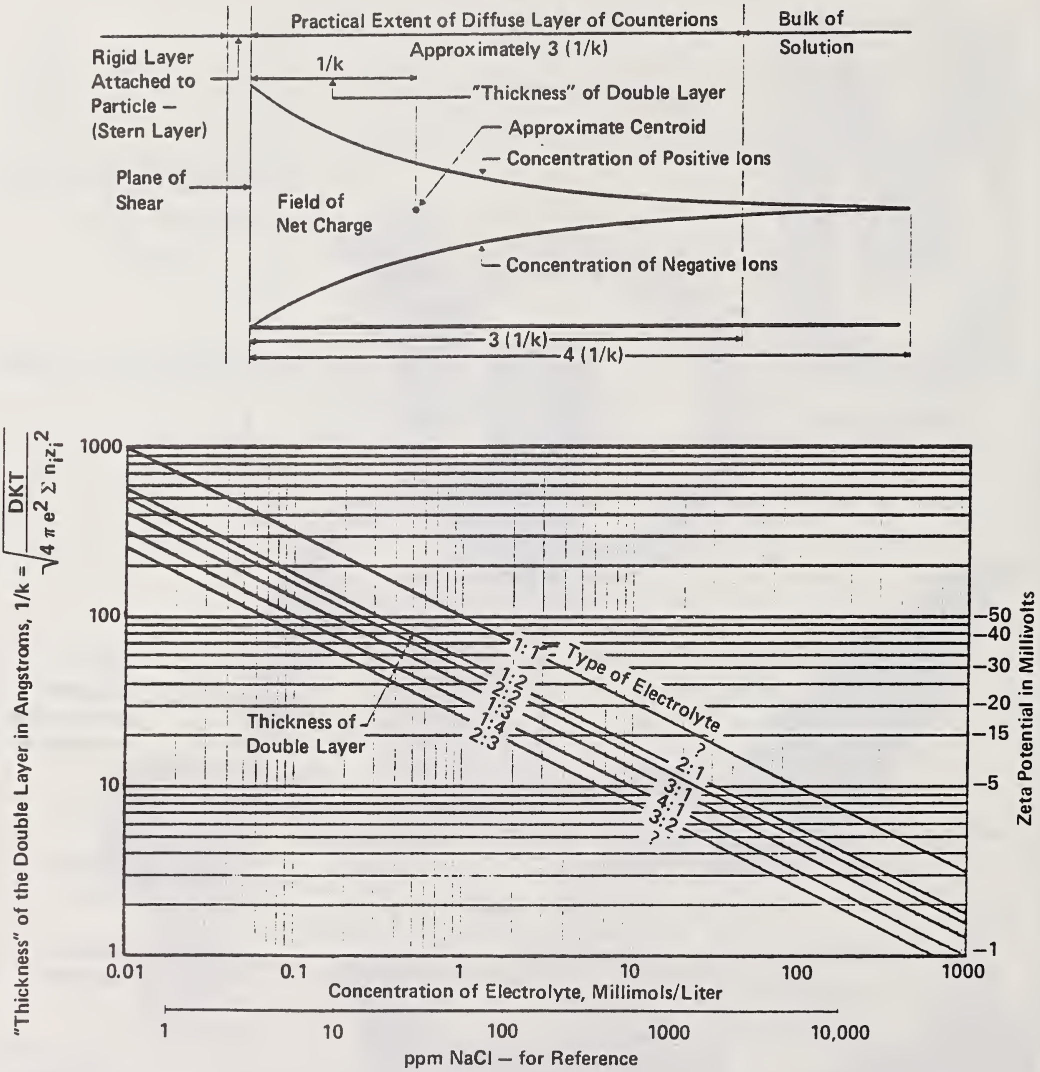
V6-Figure 6

Concept of the Zeta Potential


(Net)
Electro–
Negative
Particle
Nernst Potential
Electric Potential Surrounding the Particle
Zeta Potential
Plane of Shear
Rigid Layer Attached to Particle (Stern Layer)
Bulk of Solution
Extent of Diffuse Layer of Counterions
Concentration of Positive Ions
Concentration of Negative Ions

V6-Figure 7

Effect of Ionic Strength on Thickness of Diffuse Layer



and averaged to ensure accuracy. Their error was much less than 1%. The wide differences of fluorescence between samples measured are therefore quite indicative of the relative quantities of oil in aqueous solution. Absolute values were not measured but only estimated based on a few concentration determinations on typical low levels of soluble oil. However, using external standards the fluorescence measured indicated oil in solution to be in parts per million up to fractions of a percent, that was appreciable quantity that could quantitatively affect flotation.

11. Electrophoretic Studies

Electrophoretic studies were carried out using a three compartment cell. The centre section containing tar sands mixed with water was separated from the end sections containing the electrodes in distilled water by very fine sintered glass diaphragms (Figure 8). A constant 400 volts was maintained across the electrodes. The current was observed to increase with time indicating the transport of ions into the end compartments. The current passed through a maximum and then decreased to almost the original value, presumably when the center section has become denuded of ions, see example in Figure 8. Maximum currents were significantly different for different tar sands. The anode compartment becomes highly acid and the cathode compartment becomes highly alkaline. Evolution of hydrogen and oxygen occur slowly at the respective electrodes. The compartment solutions were withdrawn and analyzed for ions. When stirring was stopped, the sand and oil particles settled and layers were observed on the glass filters. One layer was negatively clay and the other was a green (ferrous) precipitate which on removal rapidly oxidized to red (ferric) precipitate (see Figure 8). This technique showed that significant differences existed between the soluble ions or colloids occur with different tar sands. Many separations carried out in this equipment indicated the subtle chemistry that play an important role in hot water separation and electroendoosmotic effects, such as length of pores in diaphragm and adsorption of ions on the filters are practical and theoretic complicating factors.

12. Surface Tension of Oil

A platinum, ring and tensiometer method[1] was used in this preliminary study. This method was simple and a large number of measurements were performed in a short time. Measurements at higher than ambient temperatures were carried out on preheated samples. The temperature was measured simultaneously with the surface tension, by means of a thermocouple located in or near the surface. At the very high temperatures, an infrared lamp placed about one foot from the samples and instrument shielding were used. This heating system was necessary to avoid too rapid cooling of the surface during the course of the measurement; i.e. , about one minute.

The tensiometer was first calibrated by a series of surface tension measurements at different temperatures, see Table 5. A correlation between surface tension and temperature for these liquids was plotted from data found in the literature, Figure 9. These literature values were then compared with "as measured" surface tensions at the same temperature, Figure 10. This plot shows a good agreement between both sets of data, indicated by the closeness of the point to the 45° line. The agreement at high temperatures was better than expected, as it was anticipated that the heating technique adopted might have introduced errors.

13. Interfacial Tension of Oil

The general procedure described in ASTM Standard Test D 971-50 was followed, using a platinum ring and tensiometer. High temperature measurements were made using a cell with a jacket through which hot water was circulated. This system gave surprisingly stable interfacial temperatures that were measured with a thermocouple place in the interface.

A series of measurements were also made at ambient temperatures using pure liquids of known interfacial tension. The experimental results were corrected according to the ASTM method D 971-50 and compared with literature values, Table 6 and Figure 11. The deviation from the 45° line in the plot indicates a correction factor for the instrument. This correction is very small at low interfacial tensions.

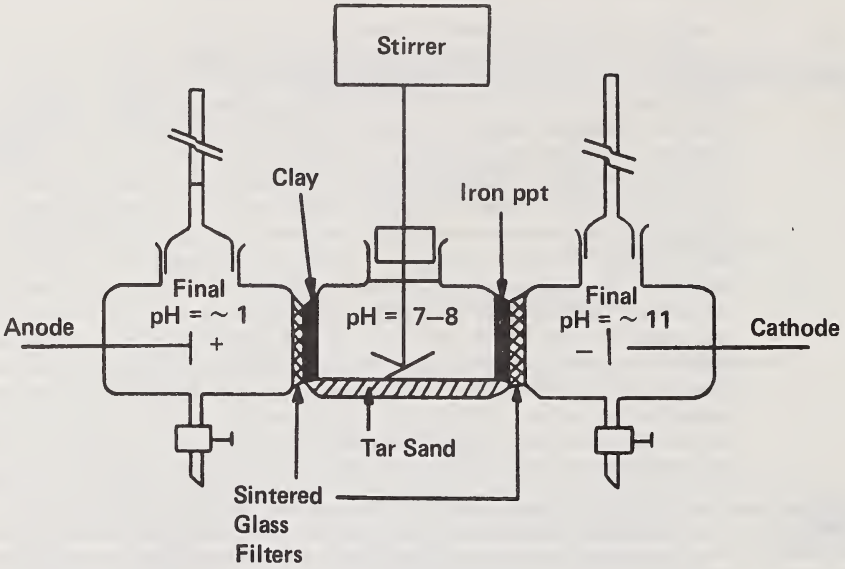
A pendant drop apparatus involving an optical bench and a heated pressure cell was used extensively in subsequent measurement of interfacial tension both at different temperatures and in contact with numerous pH and salt solutions. Unfortunately, the results of over ~100 measure-

---

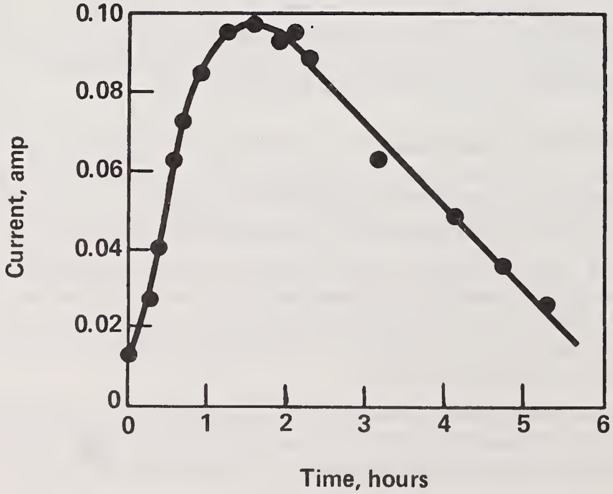
[1] *Harvey reports ring method to give results about 2.9 dynes per cm (average) higher than the drop weight method and about 1.2 dynes per cm (average) higher than the hanging drop method.*

V6-Figure 8

Electrophoretic Cell



TYPICAL CURRENT VERSUS TIME RELATIONSHIP



ments on different tars sand are lost. Essentially they confirmed the results obtained with the earlier platinum ring method as discussed above. This can be seen by the comparison of literature and experimental measurements to define the technique, Figure 12 and the correlation of ring and drop methods, Figure 13.

One additional contribution of these studies was the observations of membranes formation at the interface of the drop that could be made to remain as a buckled skin by removing the oil from the pendant drop. The modification of the properties of the membrane in the presence of different (ions) solutions lead to the postulation in the text of the importance of polyvalent ions in making the membranes rigid, that is presumed to be an important mechanism in hot water separation.

14. Contact Angles

The measurement of contact angles is difficult. The technique is described in the text and is only a rough approximation. The trend with pH, however, is considered valid.

15. Interfacial Viscosity

A Brookfield viscometer was used to measure this property of membranes formed at a solvent/solution interface, see Section 2. Although these data are lost, the effect of polyvalent ions was to increase the rigidity only slightly of Area B membranes. This supported the attachment mechanism postulated in the report.

16. Heavy Minerals

Separation of clean oil free solids using tetrabromoethane was used to define and obtain a measure of the heavy mineral content of different tar sands. Other solvents, i.e. , traillens, malonate etc. , were also used in the fraction of different density fraction. These results of these activities are discussed in detail in Section 3.

17. 5µ and Less Material

The use of 5µ material as a working basis for clay, Section 3, was arbitrarily adopted.

Assuming that Stokes Law is obeyed by irregular clay mineral particles, the settling velocity of 5µ material or less was calculated to be 0.85 cm per hour in an aqueous suspension of fines. Suspensions of fines from different tar sands, obtained by mixing tar sands with water and filtering through a 325 mesh US Screen Sieve, were settled for periods of six hours. The supernatant liquid that contained the less than 5µmaterial suspended was then withdrawn by means of a hypodermic syringe. The water was evaporated almost to dryness and the solids were washed with acetone, benzene, acetone, pyridine, acetone, water and dried in an oven. These oil-free materials were submitted for differential thermal analysis and x-ray to determine the clay minerals present.

Some fines suspension settled almost completely in the time required. The clay minerals in these suspension were presumably flocculated and only very small quantities of 5µ or less were obtained. Treatment of these suspensions with very small quantities of sodium salts; e.g. , sodium silicate, results in great dispersion of the clay minerals, although this technique was not always used. The use of sodium tripolyphosphate was not used as the phosphate anions are strongly absorbed into the clay lattices and hence can effect subsequent analysis.

18. Other Analyses

The following analyses were carried out as a service by other groups. A very brief discussion of these techniques is given below.

(a) Saturates-Aromatics-Resins-Asphaltenes (SARA)

The definition of these fractions is dependent upon the method used to carry out the separation. Essentially, three methods have been used in our studies.

(i) Original composition analyses were obtained using a silica gel adsorption technique (Humble Oil) with n-heptane to precipitate the asphaltenes.

(ii) A SARA technique was then adopted by Imperial using an activated attapulgus clay. This was similar to the Richfield Oil technique, CSA No. 17 (new classification 411), but did not use solvent recycle. N-pentane was used to precipitate the asphaltenes.

V6-Table 5

Surface Tension Measurements(1)

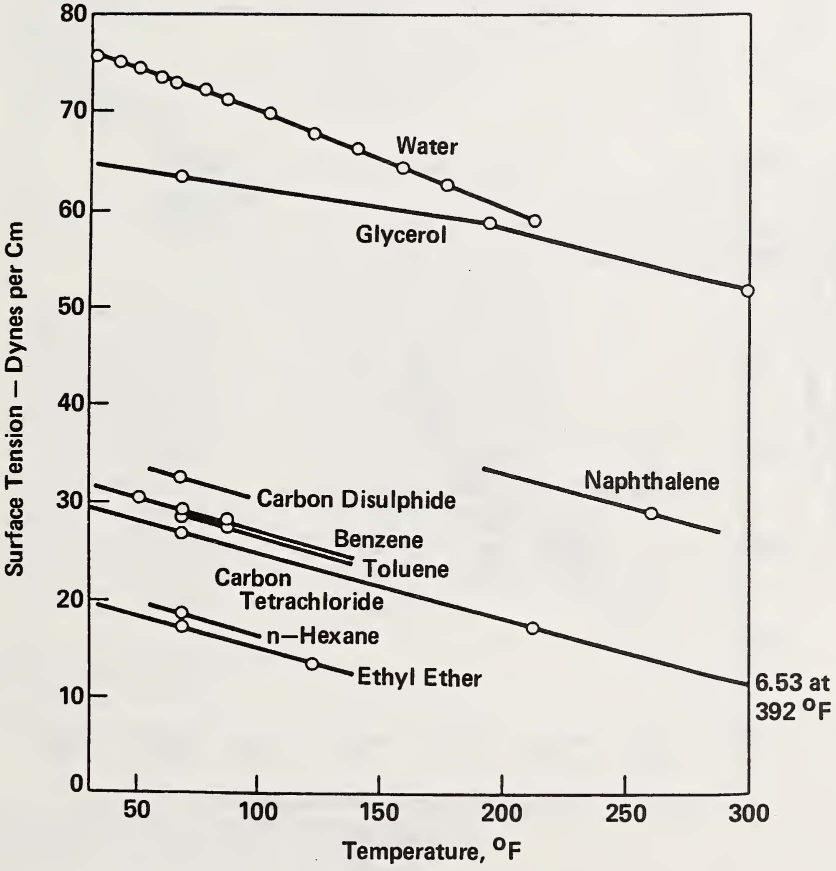
Symbol	Liquid	Surface Tension (Dynes per cm) at Temperature, °F(2)
	Ethyl Ether	17.8 at 74°; 17.3 at 50°; 18.1 at 50°.
	Carbon Tetrachloride	28.4 at 74°; 29.1 at 74°; 29.5 at 74°; 28.4 at 71°; 28.7 at 71°; 29.5 at 74°; 20.6 at 138°; 193 at 161°; 19.5 at 156°; 20.6 at 173°; 20.6 at 167°.
	Normal Hexane	18.6 at 71°; 18.6 at 71°.
	Benzene	28.9 at 71°; 29.4 at 71°; 29.3 at 71°.
	Toluene	28.7 at 71°; 29.2 at 71°; 28.5 at 71°.
	Carbon Disulphide	32.9 at 71°; 33.0 at 71°.
	Glycerol	66.0 at 71°; 66.1 at 71°; 58.1 at 165°; 58.6 at 150°; 53.3 at 285°; 56.5 at 250°; 56.4 at 250°; 55.0 at 265°; 65.7 at 75°.
	Naphthalene	32.1 at 175°; 32.7 at 175°.
	Oil from Tar Sand	37.1 at 67°; 35.0 at 69°; 35.3 at 70°; 34.8 at 72°; 35.0 at 72°; 35.6 at 72°; 34.7 at 74°; 35.3 at 75°; 34.5 at 76°; 29.8 at 85°; 30.1 at 86°; 34.0 at 95°; 27.1 at 109°; 27.3 at 110°; 29.1 at 114°; 27.0 at 120°; 28.0 at 125°; 29.9 at 125°; 25.5 at 150°; 25.4 at 150°; 22.8 at 150°; 22.4 at 165°; 22.5 at 165°; 22.4 at 165°; 22.3 at 178°; 21.0 at 180°; 20.9 at 181°; 20.1 at 182°; 19.3 at 190°; 18.9 at 190°; 18.9 at 190°; 20.9 at 191°; 20.0 at 195°; 21.0 at 198°; 20.0 at 204°; 20.5 at 210°; 19.2 at 220°; 17.4 at 230°; 18.2 at 255°; 18.0 at 254°.
	20% Oil in Benzene	24.6 at 70°; 24.7 at 70°; 24.7 at 70°.
	20% Oil in Toluene	24.5 at 72°; 24.1 at 72°; 24.0 at 72°; 24.7 at 68°; 25.1 at 75°.
	40% Oil in Benzene	25.3 at 70°; 25.3 at 70°; 25.8 at 70°.
	40% Oil in Toluene	24.0 at 72°; 23.9 at 70°; 24.4 at 73°.
	60% Oil in Benzene	28.5 at 71°; 29.9 at 71°; 29.3 at 71°; 29.8 at 71°; 30.0 at 71°.
	60% Oil in Toluene	23.6 at 72°; 23.2 at 72°; 23.9 at 72°; 23.6 at 72°;
	80% Oil in Benzene	32.1 at 71°; 32.1 at 71°; 32.6 at 71°; 32.6 at 71°; 32.3 at 71°.
	80% Oil in Toluene	29.7 at 68°; 30.4 at 68°; 29.5 at 68°; 30.5 at 68°.
	90% Oil in Benzene	32.9 at 71°; 33.5 at 71°; 33.6 at 71°; 33.5 at 71°; 33.8 at 71°.
	90% Oil in Toluene	33.6 at 75°; 32.0 at 68°.
	95% Oil in Toluene	33.6 at 72°; 34.1 at 72°; 33.0 at 72°; 33.6 at 72°; 33.7 at 75°.
	Water	72.5 at 70°; 72.2 at 71°; 72.5 at 70°; 72.3 at 72°.

(1) Using the ring method. ASTM Standard Test D971-50.

(2) High temperature measurements carried out with preheated sample and temperature measured by a thermocouple in the surface.

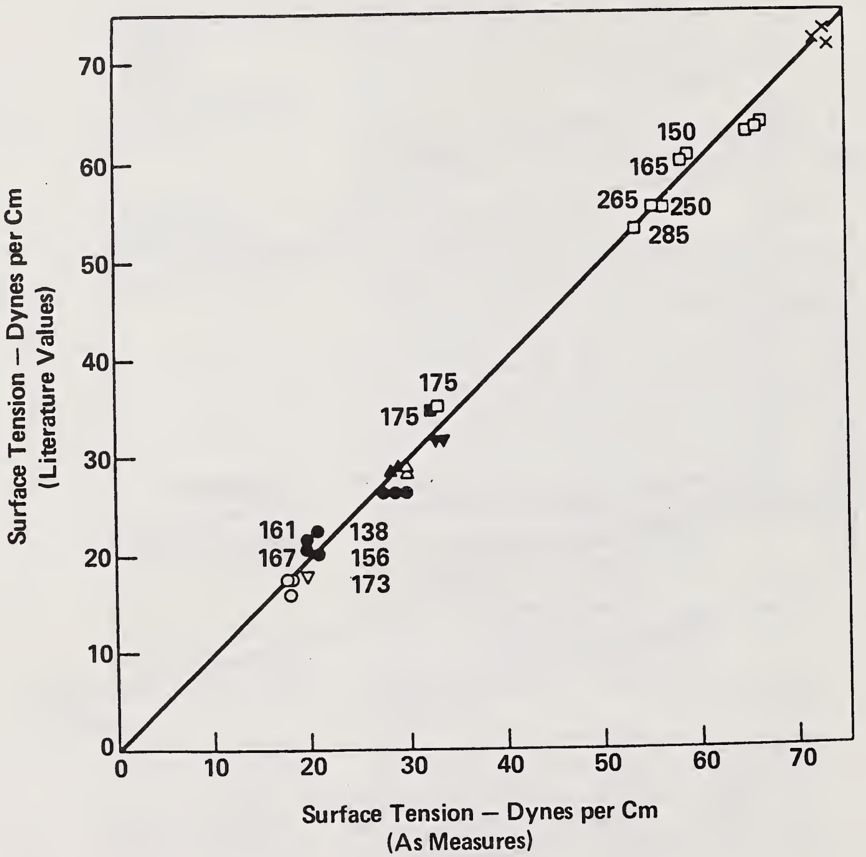
V6-Figure 9

Surface Tension Versus Temperature Correlation for Liquids Used in Instrument Calibration (Literature Values Mostly from Handbook of Chemistry and Physics)



V6-Figure 10

Literature Versus Measured Surface Tensions (Symbols and Data - See Table 6. High Temperature, °F, Measurements Shown Numerically)



V6-Table 6

Interfacial Tension Measurements(1)

Symbol	Liquid	Interfacial Tension (Dynes per cm) against Distilled Water at Temperature, °F		
	------ Corrected Values at 75°F(2) ------		Average	Literature(4) Values
	Ethyl Ether	7.5; 7.5; 8.7; 8.4; 8.2;	8.1	10.7
	Normal Hexane	41.8; 46.3; 45.1; 48.2; 43.9	45.1	51.1
	Benzene	26.8; 26.1; 27.8; 27.5;	27.0	35.0
	Toluene	27.4; 28.0; 29.3;	28.2	-
	Normal Octane	42.5; 45.9;	44.2	50.8
	------	Uncorrected Values(3) ------		
	Oil from Tar Sand	6.2 at 170°; 1.7 at 201°; 1.8 at 197°; 4.2 at 162°; 2.6 at 162°; 2.1 at 182°; 1.5 at 171°; 6.4 at 148°; 11.8 at 100°; 11.9 at 94°; 5.6 at 120°; 6.3 at 141°		
	20% Oil in Benzene	23.3 at 77°; 22.6 at 77°;		
	20% Oil in Toluene	27.3 at 75°; 25.1 at 68°;		
	40% Oil in Benzene	23.0 at 77°; 21.7 at 77°;		
	40% Oil in Toluene	25.2 at 75°; 17.7 at 68°;		
	60% Oil in Benzene	21.8 at 77°; 19.5 at 77°; 19.0 at 72°;		
	60% Oil in Toluene	19.5 at 75°; 16.5 at 68°;		
	80% Oil in Benzene	20.2 at 77°; 15.8 at 77°; 17.6 at 72°;		
	80% Oil in Toluene	18.0 at 75°; 15.8 at 68°;		
	90% Oil in Benzene	15.7 at 72°;		
	90% Oil in Toluene	16.0 at 75°; 15.0 at 68°; 15.2 at 68°;		
	95% Oil in Toluene	14.3 at 68°;		

(1) Using the ring method, ASTM Standard Test D971-50

(2) Interfacial tension (dynes per cm) = P x F
Where P = reading when film breaks and

$$F = 0.7250 + \frac{0.01452\ P}{C^2(D-d)} + 0.04534 - \frac{1679}{R/r}$$

Where C = circumference of ring; D = density of water; d = density of liquid; R = radius of ring and r = radius of wire

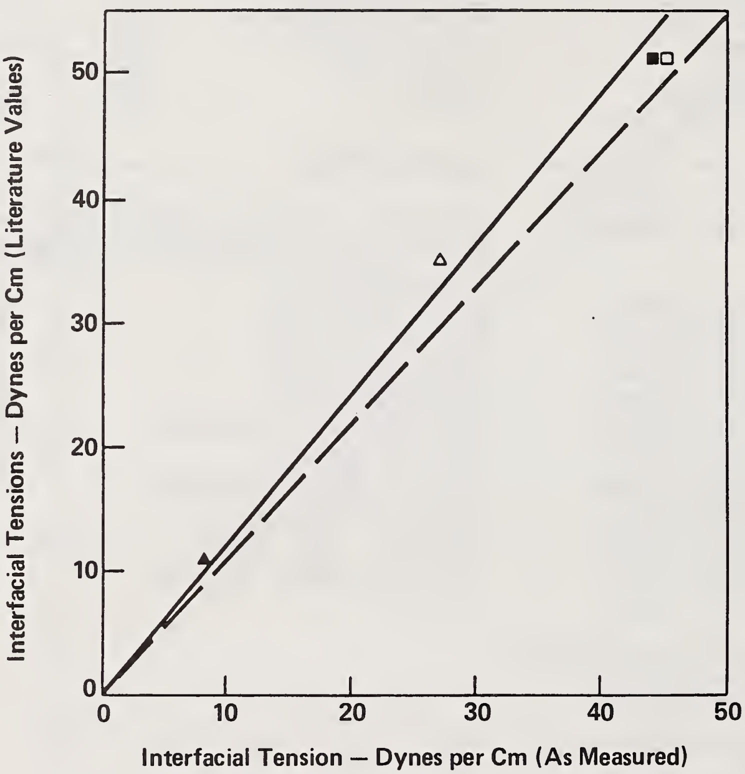
(3) As densities approach, F becomes very large and correction cannot be supplied.

(4) Mostly from Handbook of Chemistry and Physics 35th Edition, 1953-1954.

(5) High temperature measurements conducted in a hot water jacketed cell.

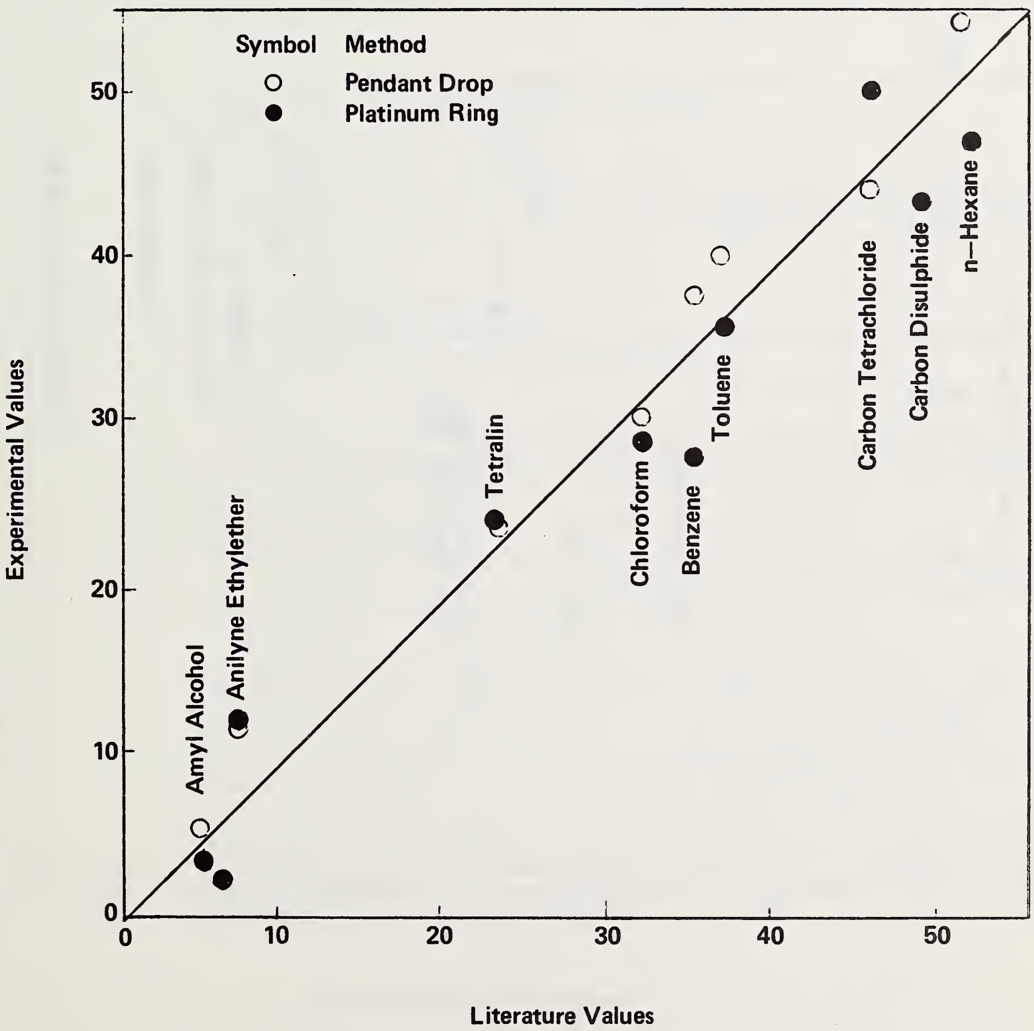
V6-Figure 11

Literature Versus Measured Interfacial Tensions (Symbols and Data - See Table 1)



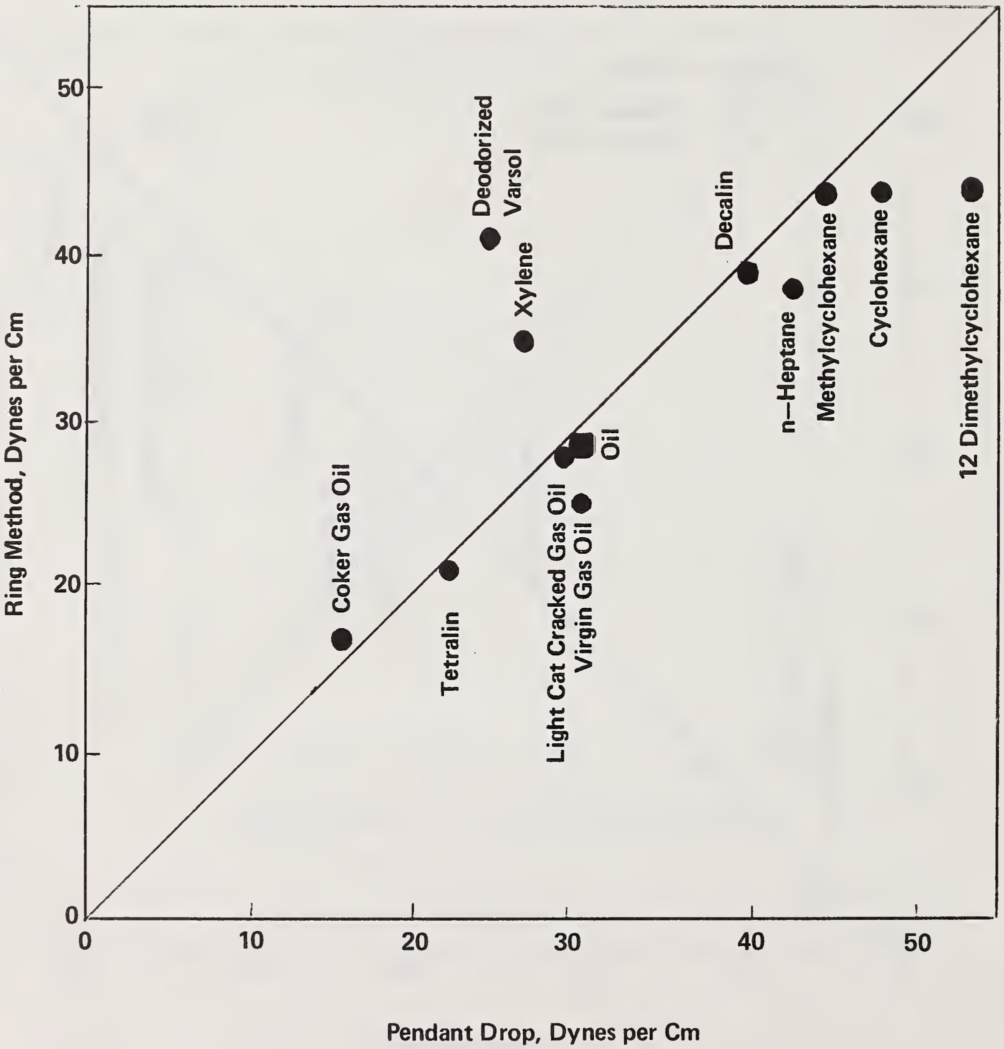
V6-Figure 12

Comparison of Literature and Experimental Measurements of Interfacial-Tension (Dynes per cm)



V6-Figure 13

Preliminary Comparison of Interfacial Tension as Measured by the Ring Method and the Pendant Drop



(iii) A simulated Richfield Oil technique, CSA N0. 17 (or 411) was tried. The results did not check Richfield Oil values too closely, perhaps due to differences in activity of the clays adsorbent.

(iv) More recent analyses have been carried out with silica gel, which is preferred on the basis of simplicity and also because the resins fraction is small and hence indicative of the most highly polar compounds. Although it can be argued that this does not represent all the resins. Clearly, a better definition of these components is required.

(b) Infrared

Infrared analyses are carried out with a Perkin-Elmer Infrared Spectrophotometer, Model 21. Runs were made either as thin films, or in CCl_4 solution with CCl_4 compensation, or as a Nujol mull.

Examples of the SARA components are shown in Figures 14-17, polar solvent extracts in Figures 18-19, and an isolated surfactant film, Figure 20.

(c) Differential Thermal Analysis

A controlled pressure and controlled atmosphere differential thermal analysis apparatus designed by Rober L. Stone Co. , Austin, Tex was used to make the measurements. The charge was 0.1 g against -alumina as a standard, using pure grade nitrogen, 120 and 10°C/minute increase in temperature.

(d) Nuclear Magnetic Resonance

Nuclear Magnetic Resonance on isolated aqueous soluble surfactants was carried out using a Varian Associates A-60 analytical N. M. R. Spectrometer.

(e) X-Ray

A Philips-Norelco X-Ray Spectrometer equipped for diffraction and fluorescence analyses. The diffraction technique was used for clay identification, and the fluorescence was used for metal determinations; e.g. , Fe.

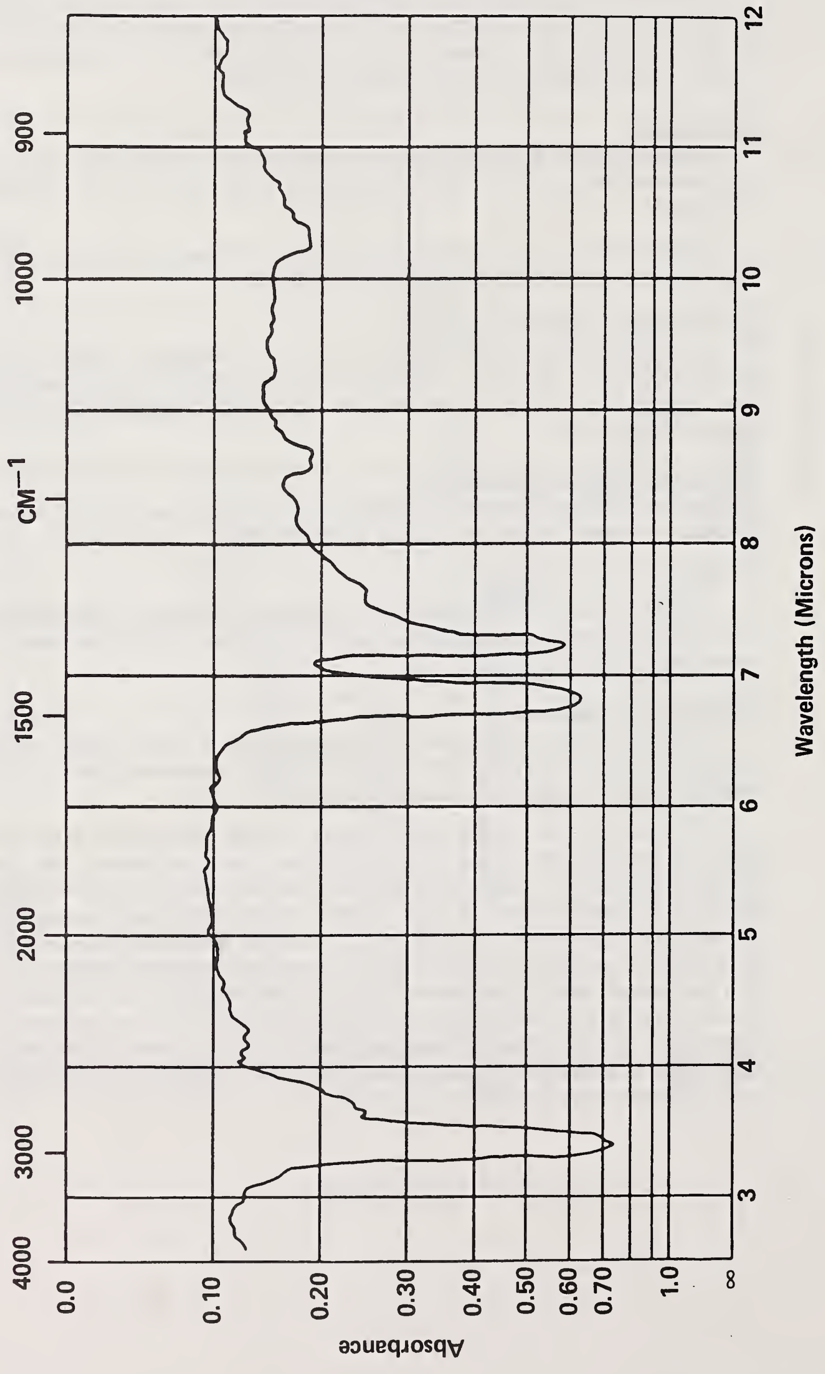
(f) Elemental Analysis

A Sargent Micro Combustion Apparatus was used to obtain carbon, hydrogen and ash values simultaneously on a semi-micro scale. Nitrogen contents were obtained using the Kjedahl method. Sulphur contents were obtained using the Leco method.

A Richfield oil technologist visited Sarnia to become acquainted with the laboratory procedure that we have been using to investigate hot water separations. Two comparisons on reproducibility between operators on samples of tar sand from both Areas B and D were completed with the results shown in Table 6. There appears to be a larger deviation in reproducing separations with Location D tar sand, but the procedure distinguishes quite readily between different types of tar sands. Further, it should be noted that the results obtained by J. W. were his first experiments using our procedure. This shows that familiarity with the laboratory extraction is not essential to distinguishing significant differences between tar sands or achieving reproducible results of about the same magnitude (± 5% oil recovery in froth) with the more difficult types of separation with poor quality tar sands. A preliminary correlation of suspended solids and oil recovery was derived, Figure 1.

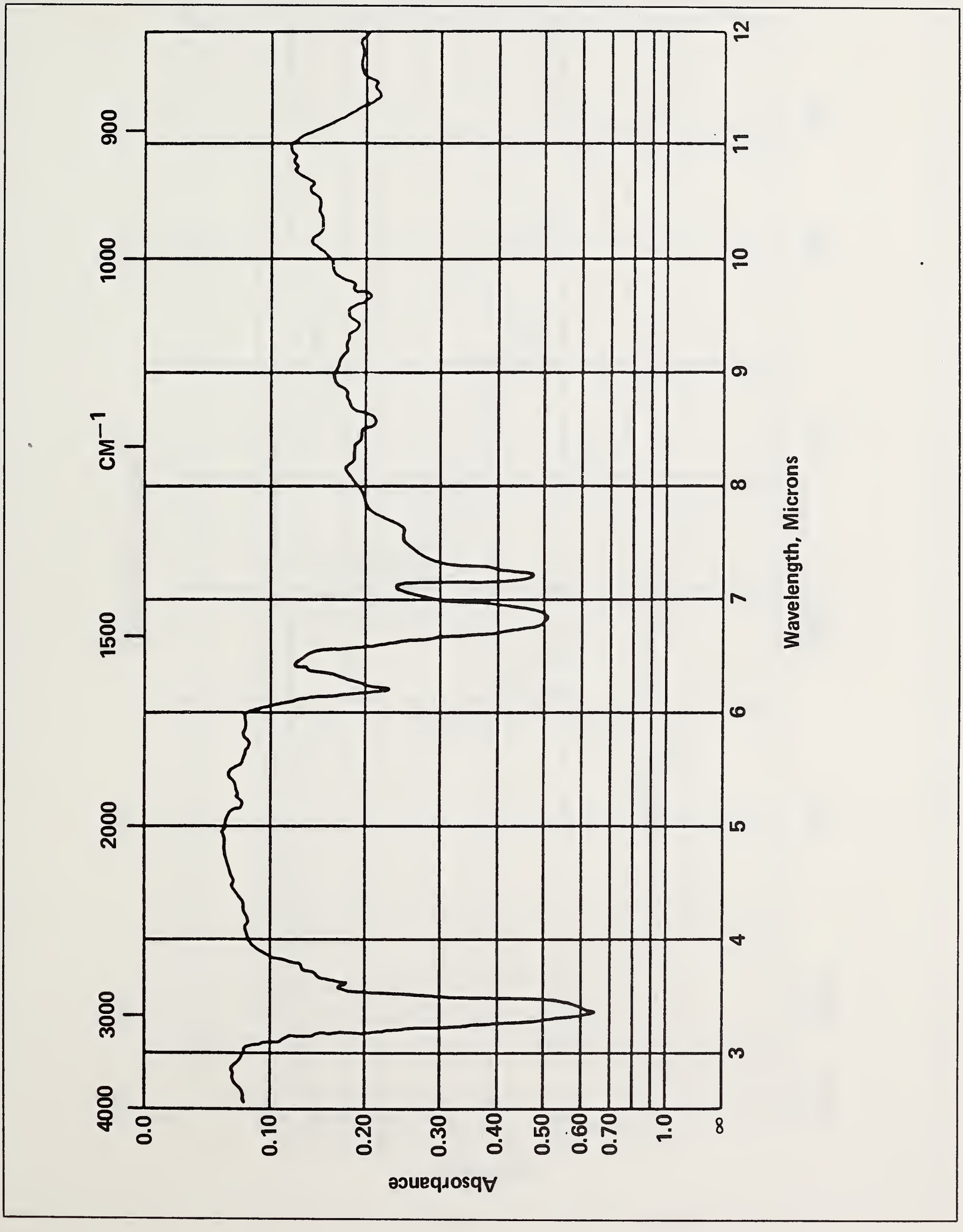
V6-Figure 14

Infra-red Adsorption Spectra of Saturates Separated from Hole 11 Tar Sand by S.A.R.A with Solvent Recycle



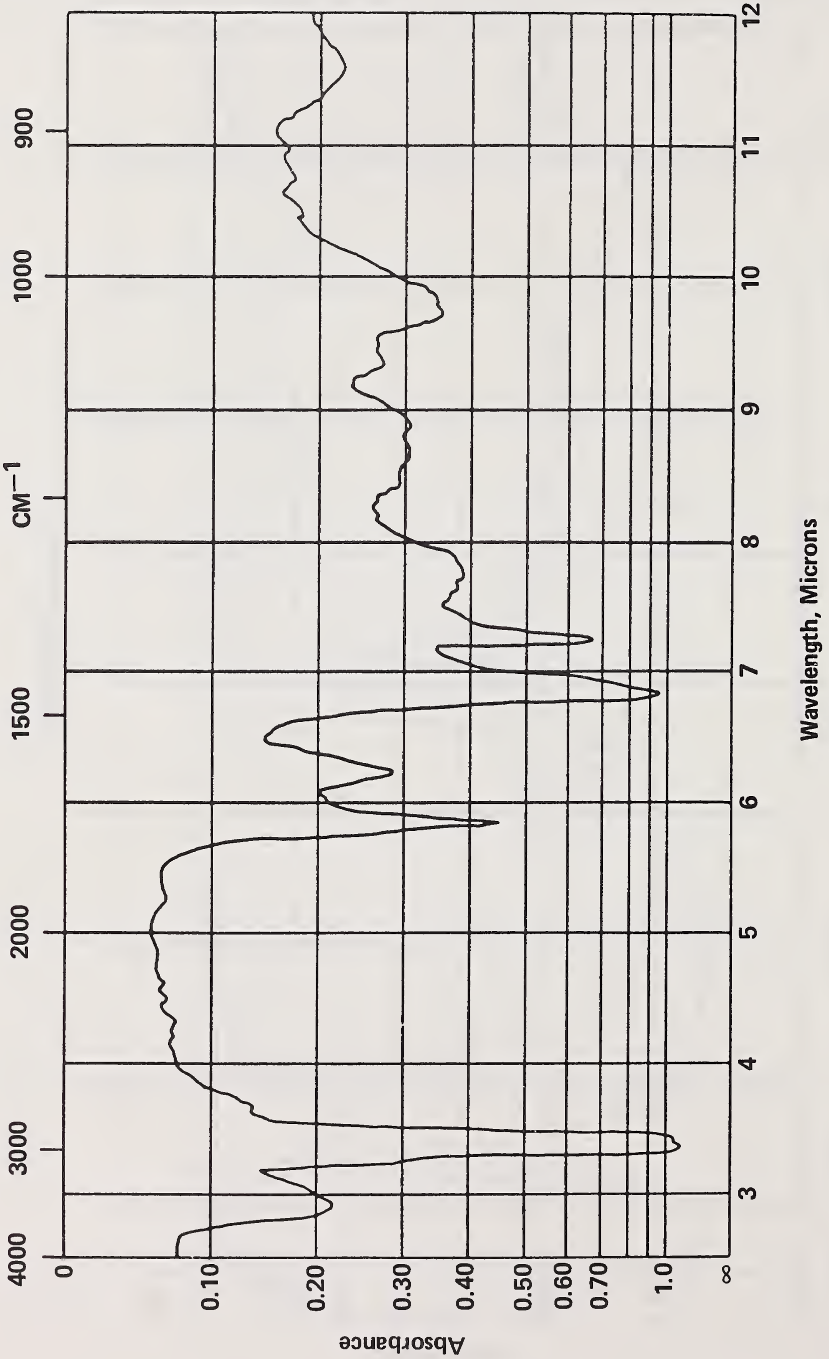
V6-Figure 15

Infra-red Adsorption Spectra of Aromatics Separated from Hole 11 Tar Sand by S.A.R.A with Solvent Recycle



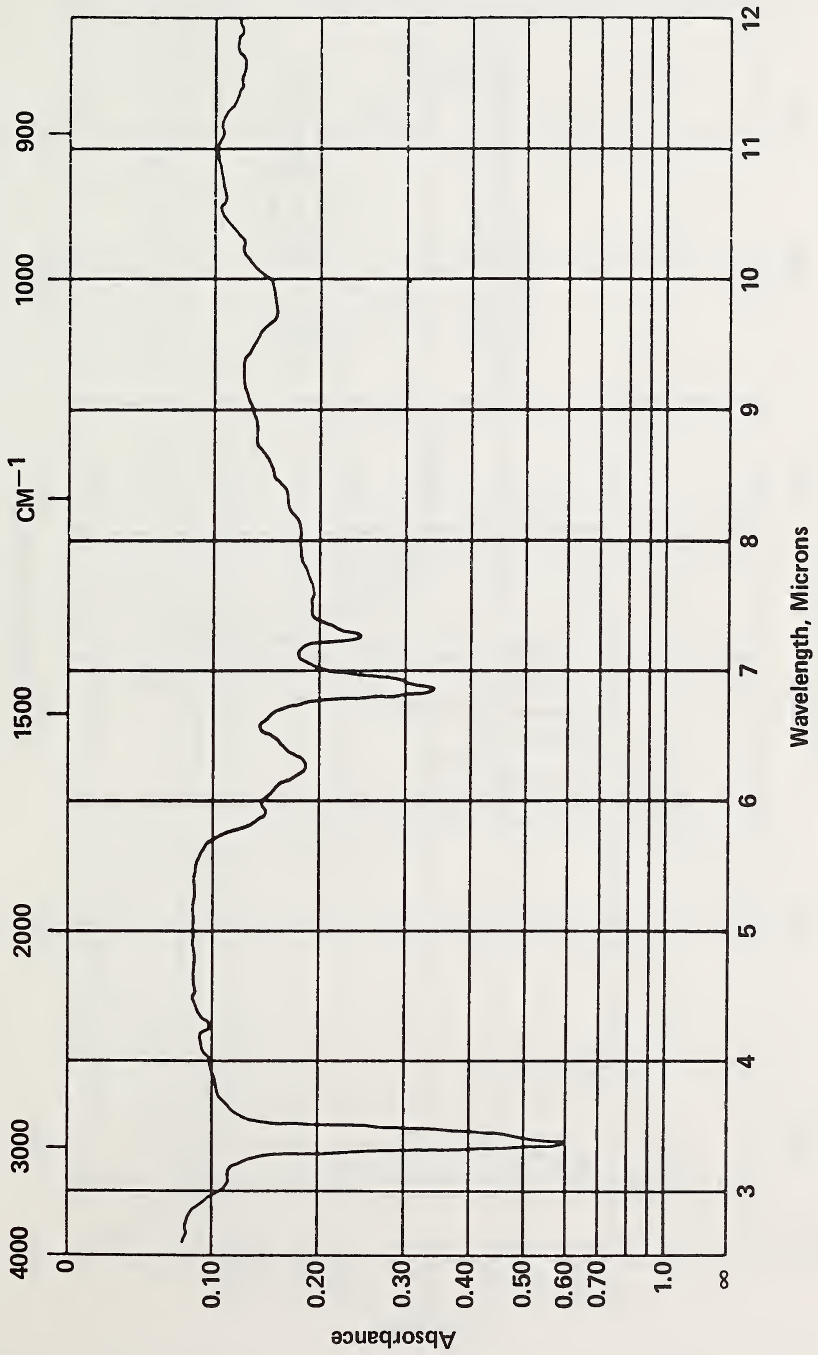
V6-Figure 16

Infra-red Adsorption Spectra of Resins Separated from Hole 11 Tar Sand by S.A.R.A with Solvent Recycle



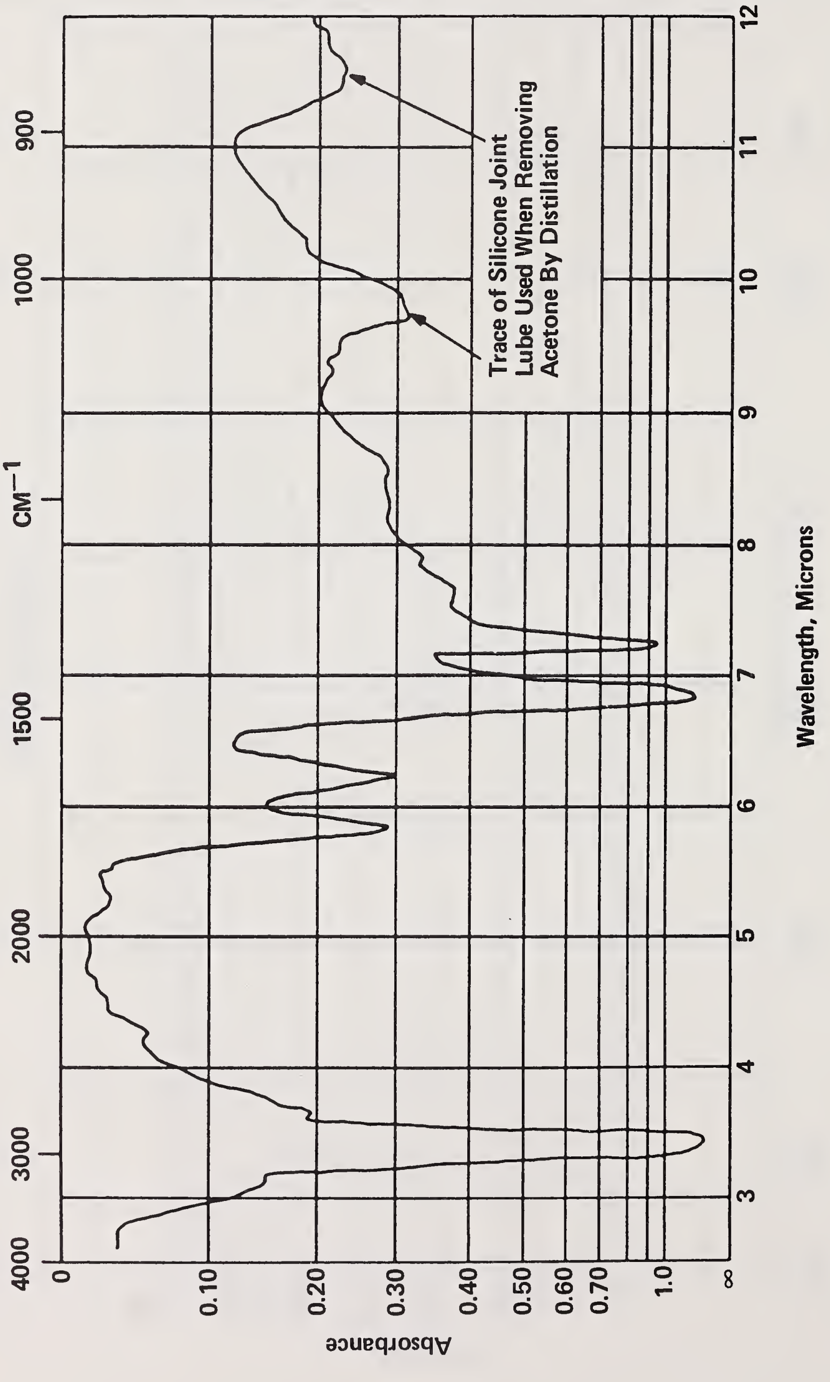
V6-Figure 17

Infra-red Adsorption Spectra of Asphaltenes Separated from Hole 11 Tar Sand by S.A.R.A with Solvent Recycle



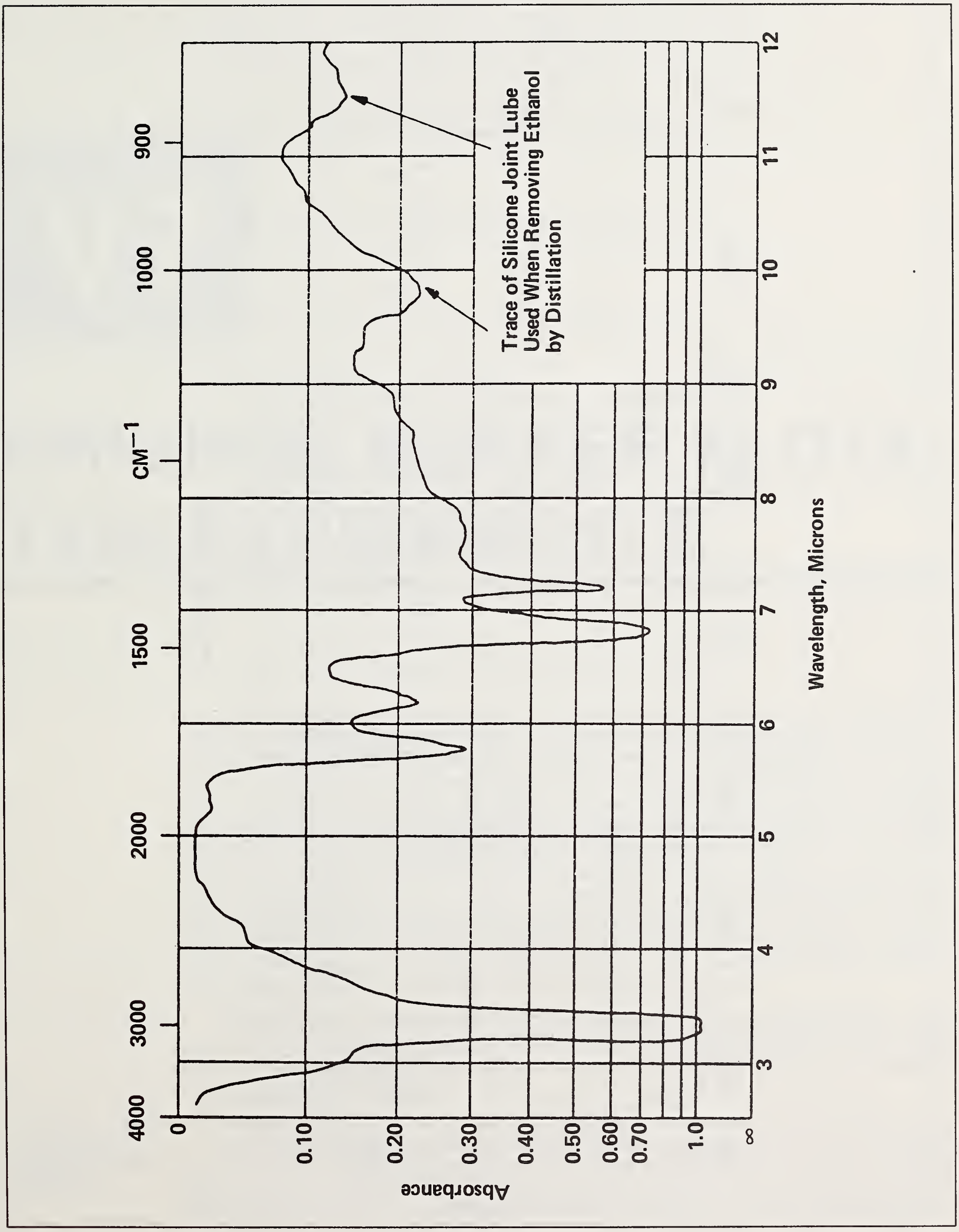
V6-Figure 18

Infra-red Adsorption spectra of Acetone Extract from Solids after Removal of Benzene Soluble Oil



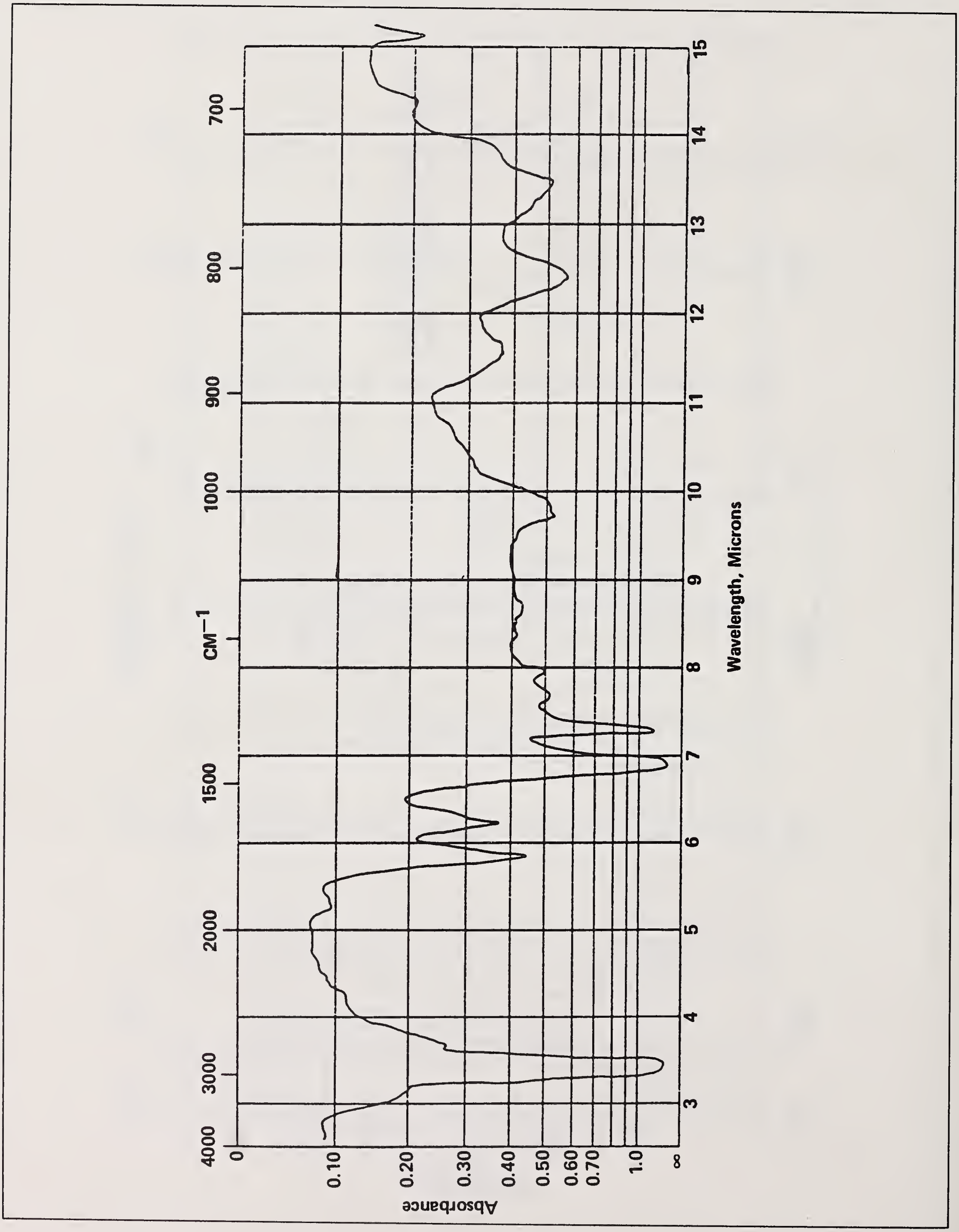
V6-Figure 19

Infra-red Spectra of an Ethanol Extract of Hole 11 Tar Sands



V6-Figure 20

Infra-red Adsorption Spectra of Surfactant Film which Peeled off from Oil Droplet under Water



V7

ORIGINAL BEAKER FLOTATION EXPERIMENTS

A beaker technique was originally developed at Sarnia to obtain a measure of the processability of tar sands in hot water flotation for comparison with the sand reduction process. A need for a laboratory extraction technique to quickly evaluate the processability of different tar sands, in the Cities Service Athabasca operations, prompted the adoption of this test. Control of process variable was not precise, but adequate for comparative work. However, this technique also proved to be a very useful research tool in obtaining some preliminary data on the process variability of different tar sands and the effect of process variables. This data is discussed in detail in this Appendix and within context these comparative results are valid. As an outcome of this work the brass pot method of hot water flotation was developed in Sarnia to give more precise process control in process variable studies. One main difference between the two techniques is that only one aeration and froth skimming was used in the beaker separations. Based on the idea of multiple-staged skimmings as the best technique from these studies, two (standard) or more aeration-skimmings were used in the brass pot extraction process.

This section has been written to preserve the original concepts and interpretation, which were made at the time and published in memoranda on completion of the work. The concepts and the inferences of these studies were substantiated and developed further by the work discussed in the bulk of the report

1. Effect of Fines With No Aeration

The first original approach to stimulate the hot water separation process used the following simple laboratory technique. A weighed amount of tar sands (100 g) was placed in a 400 ml beaker. Hot water was added to a total of 10 wt % on tar sands (dry basis) and an homogenized mass obtained by mixing with a spatula. The beaker was heated in a water bath, and steam was added to the mixture to bring the temperature rapidly up to about 180-190°F. On attaining the operating temperature steam addition was discontinued, and further mixing for two minutes was carried out. The beaker was flooded with hot water (at 180-190°F), almost to the top and the contents stirred gently. The oil froth that floated, was weighed wet, dried and weighed again to determine the water content. Any oil film remaining on the surface was floated off by further addition of water. The contents of the beaker were then gently stirred and, after less than a minute settling time, the water phase containing sludge and water-wet clay was decanted.

Sucking the water phase into a vacuum flask was also used effectively. The sand was washed with water to remove all the sludge and clay. The water phase containing sludge and water-wet clay was decanted.

Sucking the water phase into a vacuum flask was also used effectively. The sand was washed with water to remove all the sludge and clay. The water phase containing sludge was evaporated to dryness and weighed. The sand retained in the beaker was dried and weighed. Ash analyses were obtained on the dry products, i.e., froth, sludge, and sand. Weigh balances were better than 95 wt %. Products distribution and oil recoveries were computed on an output basis.

2. Modified Beaker Technique

The initial experimental technique was modified. Hot water addition in mixing for 5 minutes was increased from 10% to 20% on tar sands (dry basis) and water in flooding was reduced to 80 wt % from 300-400 wt % used initially. This was primarily to reduce the amount of process water and to simulate a 'denser' phase operation. Steam was omitted from the preheating stage as agitation was too violent, temperature control difficult, and to eliminate the possibility of any un-realistic results that might occur such as clay-oil-water emulsion formation. Temperature was controlled by means of a water bath.

After flooding with water and mixing with a spatula for two minutes, the froth was removed by scraping it up the side of the beaker. This proved to be a very effective technique and if performed correctly included little or no free water with the froth and left only a surface film of oil of negligible weight on the water.

After skimming, the sand-oil-water mixture was stirred with a sintered glass tube supplying the dispersing air at 0.5 cubic feet per hour through the system. Skimming of this second oil froth was performed as discussed above. The froth was recovered directly into an extraction cup and extracted with toluene in a Soxhlet separator. The water phases were analyzed as in Appendix (A) Section 2-6. In summary, the procedure was as outlined in Table V7-1.

V7-Table 1

Beaker Procedure

- a. Weigh out 100 g tar sand in a 600 ml tared beaker.
- b. Add 20 g of hot water
- c. Mix at 180oF for 5 minutes
- d. Flood the slurry with 60 g of hot water.
- e. Stir for 5 minutes with aeration tube dispersing air at a fixed rate - use 0.5 SCF/Hr/Lb tar sand.
- f. Remove aerator and skim froth directly into soxhlet cup to be used in the analytical procedure.
- g. Weigh beaker, spatulas and aerator before and after cleaning surface oil contamination to account for oil "loss".
- h. Add 30 g fresh water and stir beaker contents. Settle for half a minute. Decant water phase. Repeat twice using fresh water addition to wash sand free of "clay" and sludge.
- i. Evaporate decantings to dryness and ash. Use part in soxhlet extraction if sufficient sludge was obtained, i.e. about 20 g or greater, to give better oil balances.

- j. Dry the sand in the oven. Homogenize dry sample and ash. Soxhlet extract part and ash part of the sample.
- If this procedure was carried out carefully by well-trained and competent personnel, good reproducibility of results would be obtained.

3. Training

The most critical part of the procedure is the skimming of froth, and accounting for oil loss. Thus, the approach adopted in training was to first give a general introduction and then to carry out a number of separations on different types of tar sands. Because the apparatus was shared by the operators, the analytical check procedures, e.g. soxhlet extraction of "sludge", were not carried out. Thus, the preliminary comparisons were concerned with obtaining only approximate yields and oil recoveries and more with the learning of the separation technique with different quality tar sands.

Separation results with a good quality tar sand are shown in Table 7-2. Good agreement was obtained between operators throughout the series of tests. CLeaning of the beaker to establish froth loss is important. Any oil remaining on the beaker will result in a higher oil content of the sand.

Preliminary comparisons of extractions with augered samples from location "D" are shown in Tables V7-3 and V7-4. It was apparent that although decanting is fairly reproducible with high clay content tar sands, dilution with water prior to decanting would have probably given more reproducible results, and improved oil recoveries by avoiding the carry-over of fine sand into the decantings. Soxhlet extractions of the sludge should have been carried out in these experiments to give more accurate oil recoveries.

Comparing the results in Tables V7-3 and V7-4 on these tar sands obtained from Auger 9 x 1 and 9 x 2 holes of 10-15 ft apart, it can be seen that, in general, lower oil recoveries were obtained with Location "D" tar sand, which had been "disturbed" or "moved" about a year and a half ago by bulldozing.

A final comparison was made to check out the operators using the test procedure and under comparable conditions, i.e. similar improvised apparatus, times of skimming, water addition and decanting rates, and the same analytical procedures. The results shown in Table V7-5 are for a feed. It is interesting that although the procedure is reproducible between operators, it is important to adhere carefully to the method to obtain comparable results. Check programs should be part of laboratory procedure on selected tar sand samples over a wide range of compositions. Reproducibility and accuracy of the test could be greatly improved by closely controlled laboratory conditions and analytical procedures with trained operators.

A Richfield oil technologist visited Sarnia to become acquainted with the laboratory procedure that we have been using to investigate hot water separations. Two comparisons on reproducibility between operators on samples of tar sand form both Areas B and D were completed with the results shown in Table V7-6. There appears to be a larger deviation in reproducing separations with Location D tar sand, but the procedure distinguishes quite readily between different types of tar sands. Further, it should be noted that the results obtained by J.W. were his first experiments using our procedure. This shows that familiarity with the laboratory extraction is not essential to distinguishing significant differences between tar sands or achieving reproducible results of about the same magnitude (=- 5% oil recovery in froth) with the more difficult types of separation with poor quality tar sands

A preliminary correlation of suspended solids and oil recovery was derived, Figure V7-1.

V7-Table 2

Preliminary Laboratory Extraction Comparison Using Good Quality Tar Sand

(A Fresh Tar Sand from Area "B" containing 0.2% water, 12.9% oil and 86.9% solids was used)

Operator	------ **Imperial** ------ **(D.G.)**		------ **C.S.A.I.** ------ **(J.S.)**	
Experiment No.	**#13**	**#14**	**J 3(1)**	**J 4(1)**
Froth Composition, Wt %				
Water	33.6	33.8	32.3	34.6
Solids	9.6	9.2	10.4	8.8
Oil	56.8	57.0	57.3	56.6
Yields, Wt %(1) (Water Free Basis)				
Froth	14.9	15.4	14.7	13.9
Sludge	3.1	2.2	1.8	2.0
Sand	82.0	82.4	83.5	84.1
Oil Recoveries, Wt %, In (Output)				
Froth	96.6	96.9	95.9	95.0
Sludge	1.8	1.6	1.7	1.8
Sand	1.6	1.5	2.4	3.2
Material Recovery, Wt % (Water Free Basis)				
	99.6	99.7	99.5	99.3

(1) Previous experiments (J1 and J2) showed high solids in froth not enough mixing for slurry at 180°F.

V7-Table 3

Preliminary Laboratory Extraction Comparison Using an Augered Undisturbed Tar Sand from Location "D"

(Tar Sand[1] - 9 x 2 Auger Hole - 5' to 10', Location D - containing 10.3% oil, 4.3% water, 85.4% solids)

Operator	**Imperial (D.G.)**	**CSA (J.S.)**	
Experiment No.[2]	#16	J-9	J-11
Date - April	17th	19th	
Froth Composition, Wt %			
Water	47.7	51.0	47.9
Solids	11.9	14.9	14.0
Oil	40.4	34.1	38.1
Yields, Wt % (Water Free Basis)			
Froth	5.0	3.7	4.4
Sludge	34.4	33.8	20.2
Sand	60.6	62.5	75.4
Oil Recovery, Wt % In (Output)			
Froth	47.0	36.0	34.5
Sludge	51.1	52.7	50.0
Sand	1.9	11.3	15.5
Oil in Oil Phase, Wt % (Input)	36.0	23.7	29.8
Material Recovery, Wt % (Water Free Basis)	99.2	97.6	98.8

(1) Spot sample taken from homogenized large batch

(2) Dilution prior to decanting and Soxhlet extraction of sludge were not used in these tests.

V7-Table 4

Laboratory Extraction Comparison Using Augered "Disturbed" Tar Sands from Location D

(Tar Sand(1) from #9 x 1 Auger Hole - 5' to 10' Location D - containing 3.6% water, 11.3% oil and 85.1% solids, which was moved material from about 1-1/2 years ago)

Operator	**Imperial (D.G.)**	**CSAI (J.S.)**
Experiment No.(2)	#15	J-10
Froth Composition, Wt %		
Water	54.3	50.5
Solids	13.6	14.6
Oil	32.1	34.9
Yields, Wt % (Water Free Basis)		
Froth	3.9	3.4
Sludge	29.9	31.9
Sand	66.2	64.7
Oil Recoveries, Wt %, In (Output)		
Froth	32.5	29.8
Sludge	61.8	55.8
Sand	5.7	14.4
Oil in Oil Phase, Wt % (Input)	20.7	20.1
Material Recovery, Wt % (Water Free Basis)	96.9	98.8

(1) Spot sample taken from homogenized large batch
(2) Dilution prior to decanting and soxhlet extraction sludge were not used in these tests.

V7-Table 5

Final Test of Laboratory Extraction Method Run Under Comparable Conditions(1)

(Tar Sand from Location D - Bench Unit Feed IA 10 A-3)

<table>
<tr><th>Experiment</th><th>-----#20-----</th><th>------J 12----</th></tr>
<tr><td>Operator</td><td>Imperial
(D.G.)</td><td>CSAI
(J.S.)</td></tr>
<tr><td>Tar Sand Composition, Wt %</td><td></td><td></td></tr>
<tr><td>Water</td><td colspan="2">6.3</td></tr>
<tr><td>Solids</td><td colspan="2">82.4</td></tr>
<tr><td>Oil</td><td colspan="2">11.3</td></tr>
<tr><td>Froth Composition, Wt %</td><td></td><td></td></tr>
<tr><td>Water</td><td>28.7</td><td>30.2</td></tr>
<tr><td>Solids</td><td>4.6</td><td>5.0</td></tr>
<tr><td>Oil</td><td>66.7</td><td>64.8</td></tr>
<tr><td>Yields, Wt % (Water Free Basis)</td><td></td><td></td></tr>
<tr><td>Froth</td><td>10.1</td><td>10.5</td></tr>
<tr><td>Sludge</td><td>7.6</td><td>6.3</td></tr>
<tr><td>Sand</td><td>82.3</td><td>83.2</td></tr>
<tr><td>Oil Recovery, Wt %, In (Output)</td><td></td><td></td></tr>
<tr><td>Froth</td><td>77.4</td><td>80.7(2)</td></tr>
<tr><td>Sludge</td><td>17.5</td><td>15.1</td></tr>
<tr><td>Sand</td><td>5.1</td><td>4.2</td></tr>
<tr><td>Oil in Oil Phase, Wt % (Input)</td><td>77.6</td><td>81.0(2)</td></tr>
<tr><td>Total Oil Recovery, Wt % (Input)</td><td>100.4</td><td>101.8</td></tr>
<tr><td>Material Recovery, Wt % (Water Free Basis)</td><td>99.3</td><td>99.2</td></tr>
</table>

(1) Using test procedure.

(2) Higher recovery (~3%) probably due to additional stirring and skimming in an improvised heating bath while maintaining temperature.

V7-Table 6

Laboratory Extraction Comparison Between Operators on Different Tar Sands

- - - - - - - - - - - Feed Composition - - - - - - - - - - -

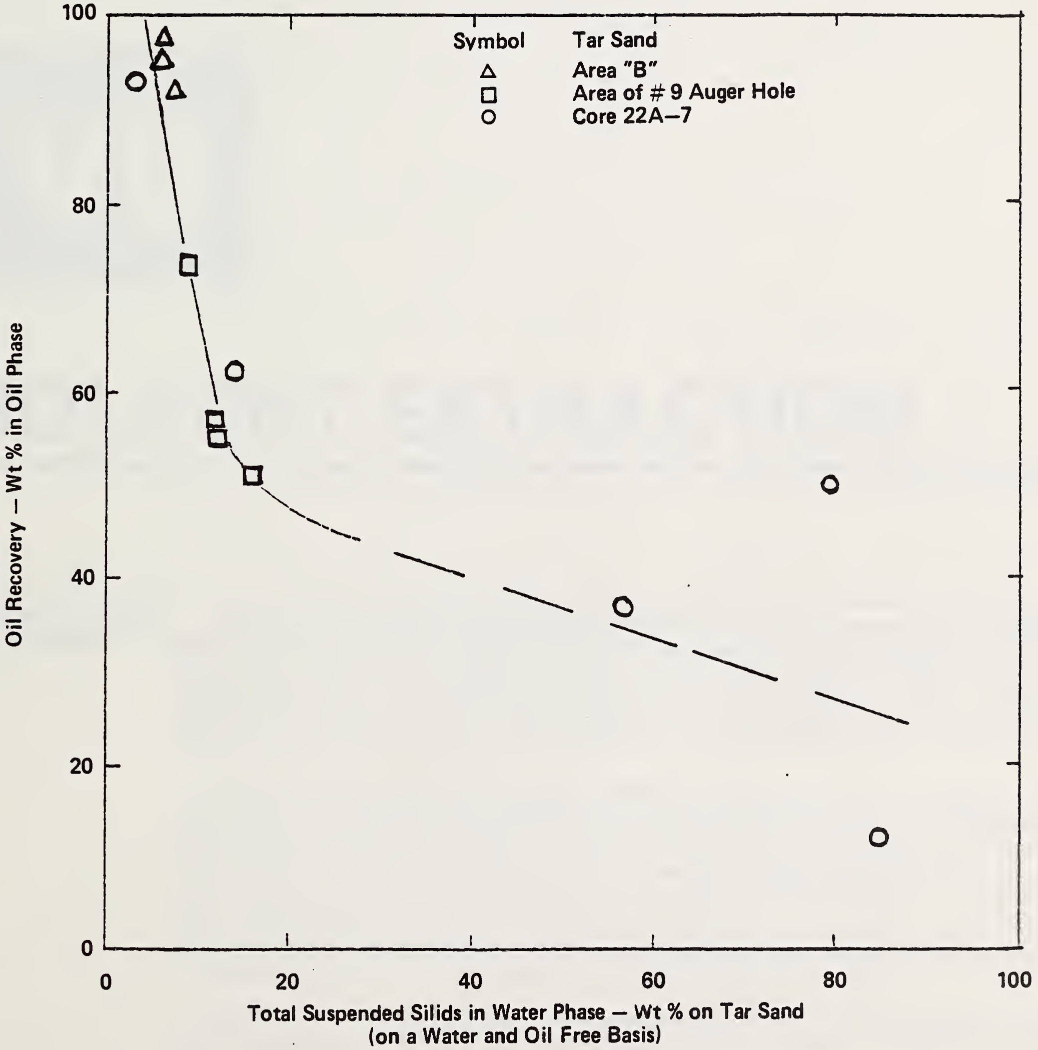
Tar Sand	**Water, Wt %**	**Solids, Wt %**	**Oil, Wt %**
Area "B"	5.8	82.4	11.8
Location "D"	8.4	83.2	8.4

- - - - - - - - - - - - - - Operator Comparison - - - - - - - - - - - - - - - - -

Operator	**Imperial (V.A.)**		**Richfield Oil (J.W.)**	
Experiment No.	**A_1**	**A_2**	**W_1**	**W_2**
Tar Sand Area	"B"	"D"	"B"	"D"
Froth Composition, Wt %				
Water	39.6	34.9	40.1	38.5
Solids	18.5	11.7	16.1	12.1
Oil	41.9	53.4	43.8	49.4
Yields, Wt % (Water Free Basis)				
Froth	16.8	4.6	16.6	5.3
Sludge	4.9	12.7	5.3	13.0
Sand	78.3	82.7	78.1	81.7
Oil Recoveries, Wt % In (Output)				
Froth	93.5	40.5	92.8	45.3
Sludge	5.3	44.3	4.5	45.5
Sand	1.2	15.3	2.6	9.4
Oil in Oil Phase, Wt % (Input)	92.8	40.7	95.6	45.5
Material Recovery, Wt % (Water Free Basis)	100.0	98.2	98.8	98.5

V7-Figure 1

A Preliminary Correlation of Oil Recovery and Total Suspended Solids in the Water Phase



V8

SOLVENT EXTRACTION

1. Electrostatic Separation

One method which has been advocated and supported by many to overcome the emulsion problem in the separation of oil from froth is by solvent dilution followed by the application of a high voltage across the emulsion phase formed to effect solids and water separation. A few exploratory experiments were carried out in the laboratory to test this approach , and to see if this technique might have any effect on the separation of tar sand directly. the result of this limited study are summarized in this section.

An area of D tar sand or a froth freshly generated in a laboratory "brass pot" separation from this tar sand were used as feeds in these experiments. When solvent was to be added initially, the feed was mixed hot with the solvent in a mortar with a pestle and poured into the apparatus shown in Figure 1. Water or fluorochemical, FC75, was first added to the apparatus in some experiments. The purpose of using the fluorochemical compound[1] was to provide a heavier clear phase to enable any change at the lower interface to be observed. The system was allowed to stand for about 15 minutes to come to equilibrium state. The voltage was then applied for about 15 minutes during which time observations were made and measurements taken.

The system , in most of the experiments, was changed stepwise by the addition of water, fluorochemical, or more solvent, and the standing and voltage application was repeated in each step.

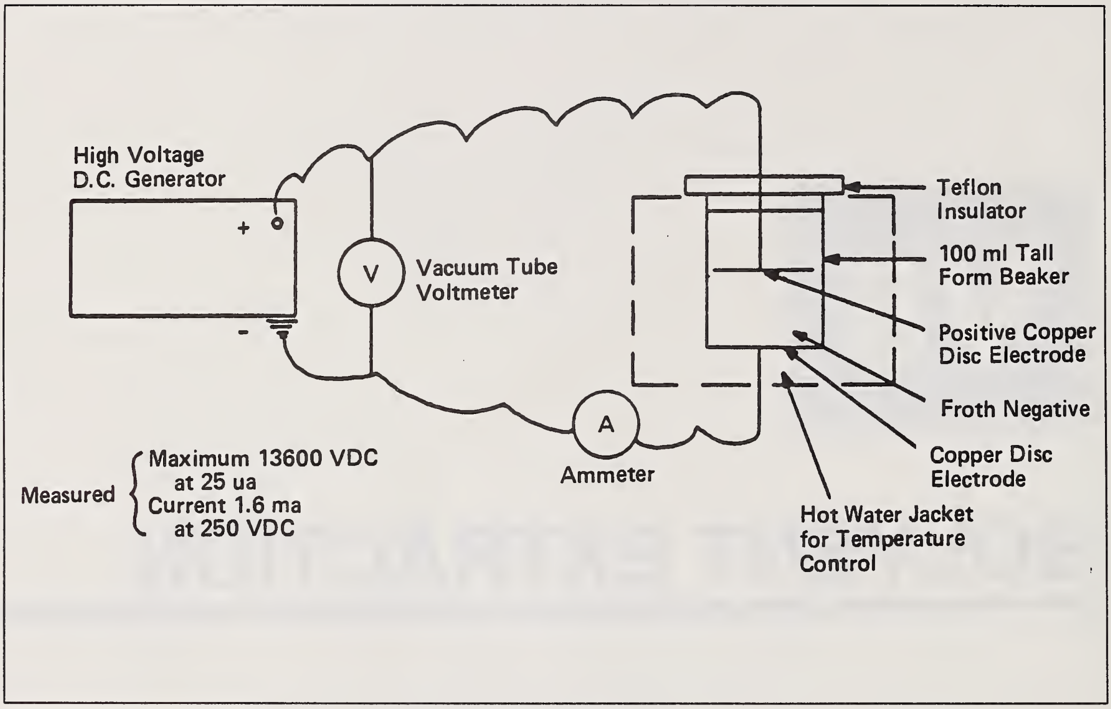
Generally, when the system was modified by the addition of solvent during an experiment, gentle stirring with a spatula for about 5 minutes was carried out to ensure good mixing of the oil and solvent present in the system.

---

[1] *A fully fluorinated cyclic ether (5 and 6 member ring) of general formula* $C_8F_{16}O$.

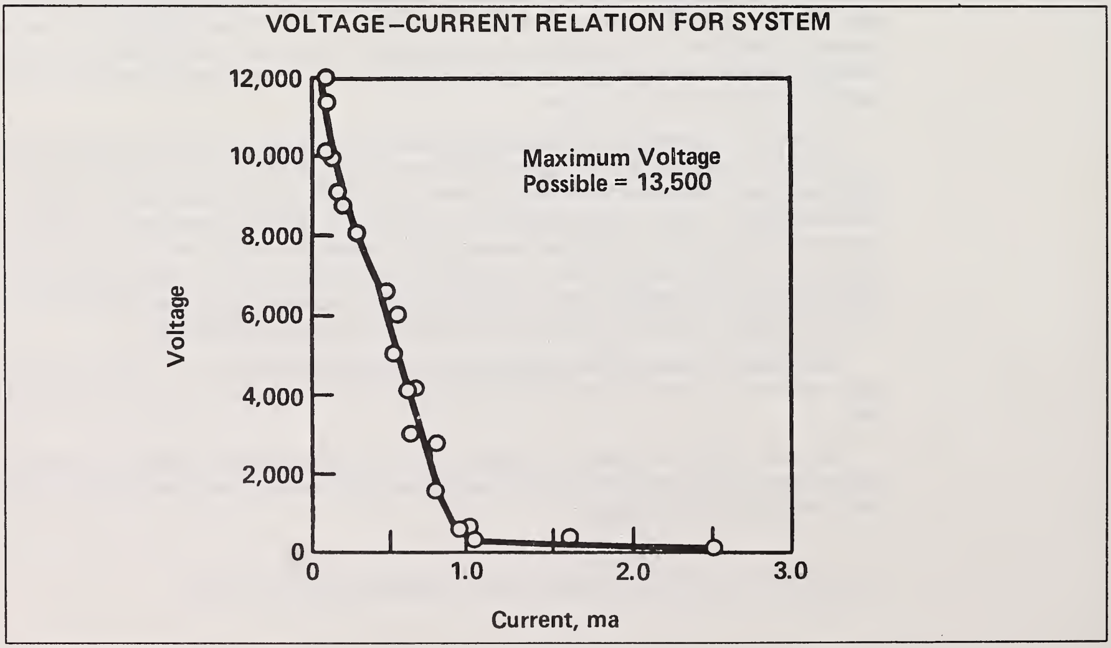
V8-Figure 1

Apparatus Used in Applying Voltage



V8-Figure 2

Appendix D Figure 5 Voltage-Current Relation for System



(a) Separation of Tar Sand

Four experiments were carried out. The results are summarized in Table 1.

No visible change occurred in the system over gravity settling in most of these experiments. However, when fluorochemical was added to the system in tow experiments, a clear separation between the oil-solvent phase and a sand phase was effected. Applying a voltage effected release of oil from the sand phase. This appeared to be caused by a slight ebullution in the fluorochemical phase, as this effect occurred independently by the polarity of the upper electrode (column 8).

The addition of water in experiments C, which would be used in a commercial operation, resulted only in lowering the voltage with no visible effect on the skin-type emulsion observed below the oil-solvent phase.

It was noted that with fresh tar sands a sludge was observed to adhere to the upper electrode when the latter was positively charged. This sludge was very small in quantity and, when dissolved in CCl4, indications were that it contained very little oil and that the water wet solids were fine sand with some clay. In the last experiment (D) with an oven dried tar sand, no deposit was observed on the upper electrode when positively charged.

These observations suggest that some "water solvated" solids, perhaps with absorbed ions, are negatively charged, which might be predicted from interfacial electrophenomena reported in the literature.

(b) Separation of Froth.

A series of experiments was carried out to investigate the application of voltage to the breaking of emulsions. The voltage-current relation found in these experiments and also with those with tar sands discussed above is shown in Figure 2. The details of these experiments are recorded in Table 2. A diagrammatic representation of these system is also shown in Figure 3.

The data showed a relationship between the steady voltage attained and the volume ratio of total oil (including fluorochemical, FC75) to water in the system . This is shown in Figure 4. It can be seen that voltages are maximized by minimizing the water content of the system. However, in all these experiments, no visible effect was observed on applying a voltage. (The results with tar sands follow a similar but not identical pattern. Presumably the sand has a surrounding film of water, which creates a larger effective conducting volume in the system.).

. It is interesting that when froth was used (experiment 1(a) symbol) essentially no voltage and high current was obtained. This indicates that the water in the froth is sufficiently continuous to conduct all the electricity available . Unfortunately, the DC voltage generator was of the electro static type so that when current was drawn , the voltage decreased . By extending this continuous phase by the addition of water, the same result was observed (experiment 1(b)).

The addition of solvent (and/or fluorochemical) resulted in higher voltages and lower current , but no visible change in the emulsion was observed over gravity settling.

As the water in the emulsion phase is probably continuous , the voltage drop is mainly across the upper the electrode in the oil-solvent phase and the oil-solvent/water interface and not across the emulsion which hangs in the conducting water phase. Theoretically, if a voltage is placed across a film of emulsion , it may be possible to break the system. However, as long as the water is sufficiently high in concentration , the emulsion is short circuited by the continuous water phase surrounding and dispersed through the emulsion. Then the voltage drop is across the oil-solvent phase.

As essentially no voltage is obtained if the water is a continuous phase, such that in the froth , and presumably in the emulsion formed with solvent dilution. Hence, complete oil separation in these cases will be extremely difficult, if not impossible , to effect on a continuous basis even using a high current-high voltage electro-technique.

V8-Table 1

Some Experiments on the Effect of Electrostatic De-emulsification of Froth with and without Solvent Dilution

Experiment[1] Number	Tar Sand[2]	Addition, Wt % on Tar Sand			Voltage Attained	Current ma	Upper Electrode Charge	Upper Electrode Deposit[4]	Visible Effect On Sep^n
		Varsol	FC75 Phase[3]	Water					
A (i)	CSA-Area D	15	0	0	500	-	+	Yes	No
B (i)	" "	15	140	0	13,000	-	+	(Note 5)	No
(ii)	" "	15	140	0	13,000	-	-	(Note 5)	No
C (i)	" "	100	0	0	5,000	0.5	+	Yes	No
(ii)	" "	100	0	0	6,500	0.45	-	No	No
(iii)	" "	100	18	0	9,000	0.21	-	No	(Note 6)
(iv)	" "	100	18	0	9,000	0.21	+	Yes	No
(v)	" "	100	18	10	5,000	-	+	Yes	No
(vi)	" "	100	18	10	4,000	0.60	-	No	No
D (i)	"Oven Dried"	100	0	0	10,000	0.16	+	No	No
(ii)	" "	100	0	0	10,000	0.18	-	No	No
(iii)	" "	100	0	0	9,000	0.20	+	No	No
(iv)	" "	100	18	0	11,500	0.08	+	No	(Note 7)
(v)	" "	100	18	0	12,000	0.07	-	No	No

(1) Each system or changed system is shown by one line of data.

(2) Contained 11% oil, 4.5% water, 6% fines and 78.5% sand.

(3) Fully fluorinated cyclic ether $C_8F_{18}O$. Structure not completely defined, either a 5 or 6 member ring containing the oxygen. Gravity of 1.75 g/cc. This was used to see if there was any settling or change in the system.

(4) The deposit in all the experiments was small (about 1-2% on tar sand). It had the appearance of sludge (i.e., sand - clay - water with very little oil).

(5) Oil refluxed to upper electrode when located in the air space just above the mixture. Some fines (including sand) appeared to be carried up and remained on the top of the electrode.

(6) Addition of the fluorochemical effected a clean separation of oil from a sand phase containing oil. Turning on the voltage resulted in the immediate release of oil from the sand phase leaving a fairly clean sand phase. This appeared to be caused by a slight "ebullition" effect in the fluorochemical.

(7) The same effect as described under Note 6 was observed, except less oil appeared to be released and more oil remained with the sand, as would be expected.

V8-Table 2

Some Experiments on the Effect of Electro-Separation of Tar Sands (Tar Sand was Premixed at 140-150 °F with 31-39 Varsol in a Motar with a Pestle for 5 minutes and transfered to the apparatus shown in Figure 1, which was maintained at about the same temperature

Froth used in these experiments was freshly generated in a laboratory dense phase separation at 185°F using a sample of Area D, Hole 9, tar sand containing 11% oil, 4.5% water, 6% fines and 78.5% sand. The froth had an average composition of 49% water, 9% solids and 42% oil. The froth was maintained at 180°F in all subsequent operations. Standing periods of about 15 minutes were employed before and during applied voltage treatment.

Experiment(1) Number	Addition, Wt % on Froth			Voltage Attained(4)	Current ma	Visible Effect On Sep^{n}
	Solvent(2) (with mixing)	Water	FC75 Phase(3)			
1 (a)	0	0	0	0	2.5	No
(b)	0	70	0	0	2.5	No
(c)	59	70	0	150	1.0	No
(d)	178	70	0	4000	-	No(7)
2	105(5)	35	0	2000	-	No(7)
3 (a)	230(5)	0	0	(10000) → 8000	0.25	No(7)
(b)	230	34	0	4000	0.6	No
(c)	230	69	0	2750	0.75	No
4 (a)	103(5)	122	0	(250) → 500	1.6 → 0.9	No
(b)	103	61(6)	0	(500) → 1500	0.9 → 0.75	No
(c)	154	61	0	(2500) → 3000	0.60	No
5 (a)	0	0	350	6000	-	No
(b)	0	0	520	9000	0.2	No
(c)	42	0	520	10000	0.15	No

(1) Each system or changed system is shown by one line of data.

(2) Light gas oil, gravity of 0.85 g/cc.

(3) Fully fluoronated cyclic ethyl $C_8F_{16}O$. Structure not completely defined, either a 5 or 6 member ring containing the oxygen. Gravity of 1.75 g/cc. This was used to see if there was any settling or change at the bottom of the aqueous-oil phase.

(4) Initial voltages are shown in parenthesis. All other voltages were maintained steady during standing period.

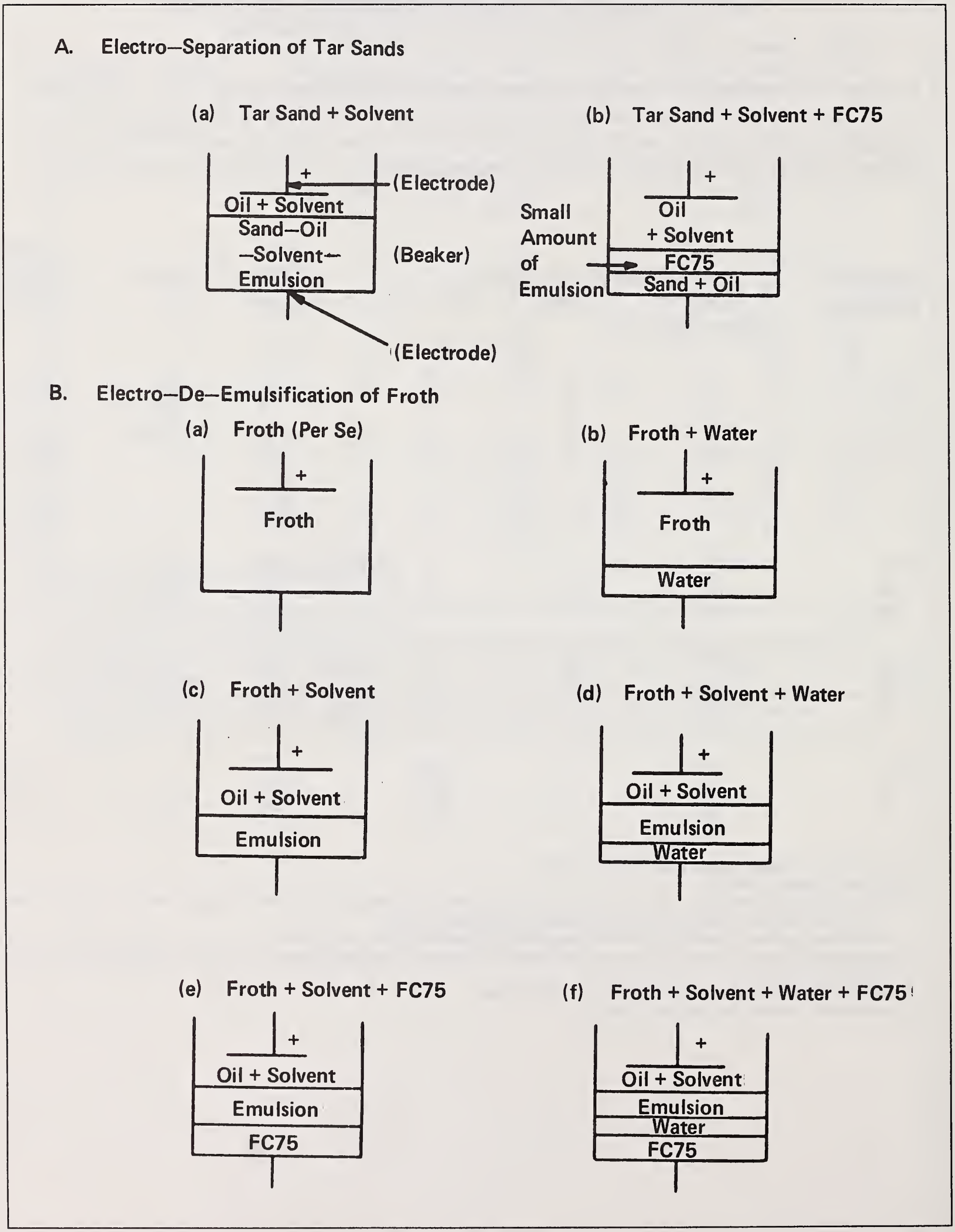
(5) Mixing was carried out for 5 minutes in a mortar and pestle at 180°F. Mixing with other solvent additions was carried out in the apparatus, Figure 1A, with a stirrer at about 120 rpm.

(6) Water was withdrawn from the lower phase with a hypodermic syringe.

(7) Small amount of emulsion on upper positive electrode.

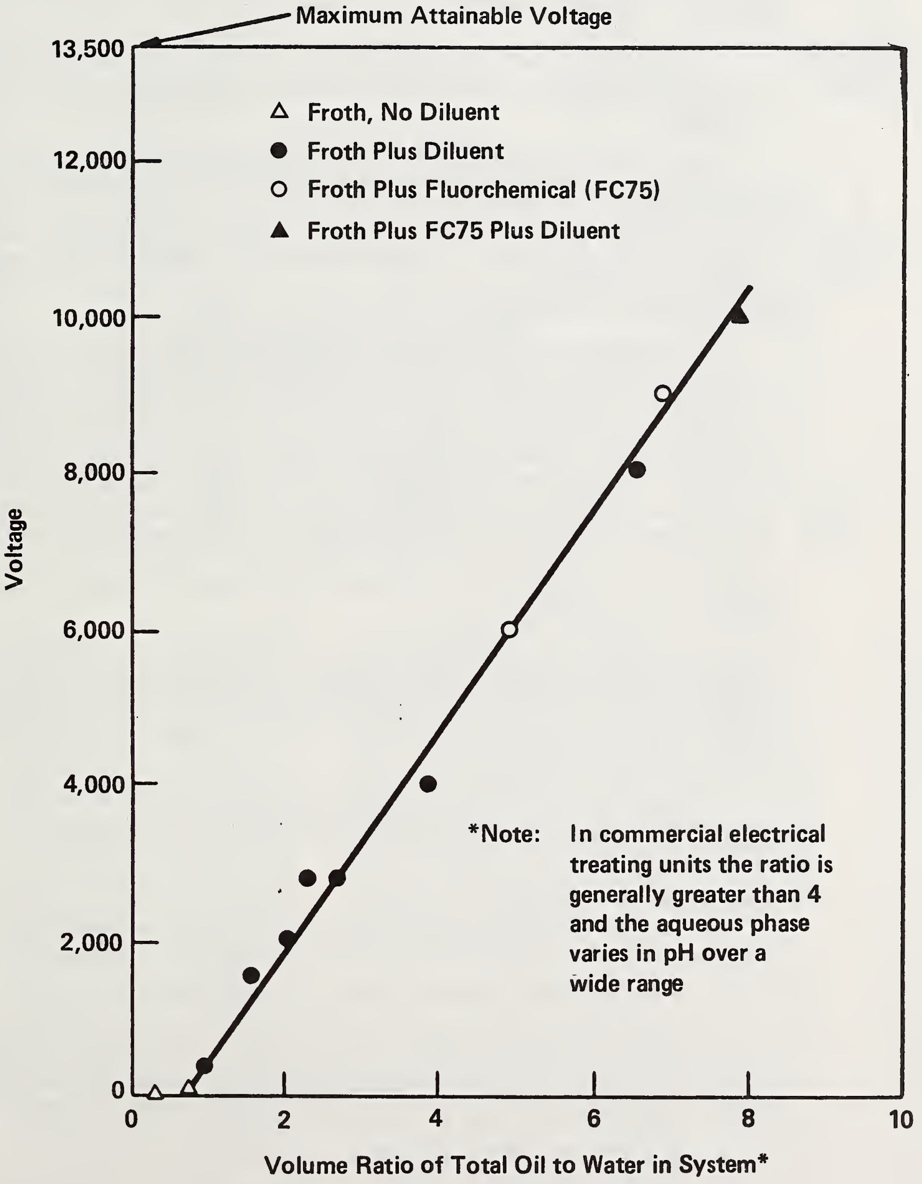
V8-Figure 3

Diagrammatic Representation of Systems Studied



V8-Figure 4

Volume Ratio of Total Oil to Water in the System Showed a General Relation with Voltage



*Note: In commercial electrical treating units the ratio is generally greater than 4 and the aqueous phase varies in pH over a wide range

(c) Summary

Within the content of these few experiments, it may be concluded that the application of voltage to;

(i) Separation of oil from bulk sand with no solvent dilution or tar sands does not appear promising or significantly different to gravity settling.

(ii) Separation of water and solids from froth with solvent dilution does not appear to be promising or significantly different to gravity settling.

2. Solvent /Dilution and Settling.

A number of experiments on solvent dilution and settling of froth (from Hot Water Flotation) and agglomerate (from Sand Reduction) generated in the laboratory from Area B type tar sands are reported here.

Two basically different approaches were used in the small scale laboratory separations. First, the weighed feed was mixed with solvent (varsol) and separated by addition of the mixture. to water. This has been termed solvent dilution. Second, the weighed feed was mixed with solvent and then decanted to recover the oil-solvent solution. This technique in some cases was repeated. Any sludge in the oil-solvent phase which settled out in 10 minutes was returned to the sludge. The remaining sludge, i.e, mixture of sand and water-oil-solvent was than separated by addition to water to generate further oil in solvent and emulsion.

In both techniques the phases were separated using a separatory funnel to collect the oil-solvent phase, an emulsion phase, and water solids phase containing some oil. These three phases were analyzed for solids, oil and water. Oil recoveries and composition of the oil phase were obtained. The general plot of oil recovery vs solvent oil ratio is shown in the text Figure 9-10. It can be seen that a minimum solvent oil ratio of about 0.7 was required to affect a substantial separation of oil and solvent phase. Higher solvent oil ratios resulted in only slightly higher oil recoveries and slightly less emulsion forming. The oil loss to the water phase decreases with higher solvent-oil ratios, as shown in the text Figure 9-11. The lower plot in this figure shows a cumulative composition of total oil phase which include the emulsion. It will be noted that a higher solvent-oil ratio gives more emulsified water although less emulsion is produced. these results are only preliminary.

It has been observed qualitatively that this approach to up grading the froth can be substantially improved by using the anhydrous technique and utilizing pH control with preferentially sodium phosphates and silicates. Perhaps surfactants may also be used to reduce the emulsion problem. However, a very thorough systematic evaluation of these variables and also rate data on settling will have to be carried out.

Reference Figure 5 for information on Laboratory Dilution Settling procedure and a Dilution and Settling Apparatus. Figure 6 shows photographs of the actual Small Scale Dilution Settling Apparatus used in the laboratory.

(a) Other Solvent Studies.

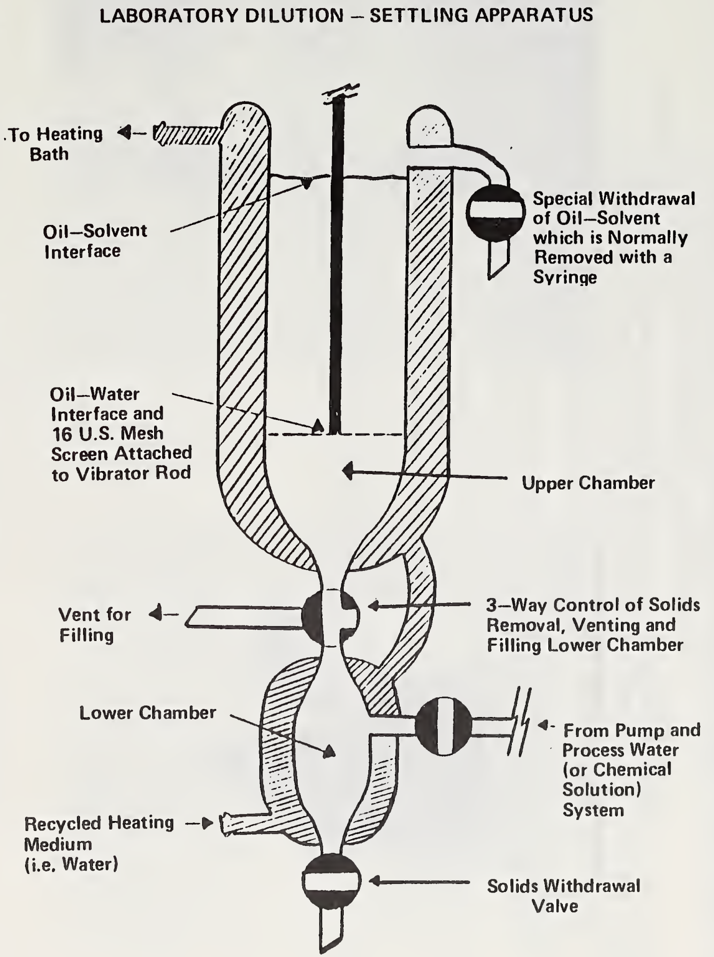
Several qualitative studies have been carried out to evaluate the results of solvent type , pH additives and organic surfactants. The following observations have been made:-

(1) Phenol, as a solvent, appears to increase the emulsion problem.

(2) In general, the hydrocarbon solvent are very similar. However, the emulsion problem appears to be less with some types than others, although other conditions are complicating, e.g temperature - viscosity. It has been observed that gas oil zene is better than n-heptane, and varsol better than gas oil from the point of view of minimizing the emulsion problem.

(3) Sodium salt addition pH control tends to reduce the emulsion problem.

(4) Sodium tripolyphosphate and organic surfactants with HLB of 6-8 and 16-8 are most effective in reducing the emulsion problem.


LABORATORY DILUTION — SETTLING APPARATUS
To Heating Bath
Oil—Solvent Interface
Oil—Water Interface and 16 U.S. Mesh Screen Attached to Vibrator Rod
Vent for Filling
Lower Chamber
Recycled Heating Medium (i.e. Water)
Special Withdrawal of Oil—Solvent which is Normally Removed with a Syringe
Upper Chamber
3—Way Control of Solids Removal, Venting and Filling Lower Chamber
From Pump and Process Water (or Chemical Solution) System
Solids Withdrawal Valve

V8-Figure 5

A Laboratory Dilution - Settling Apparatus

(1) Operation

A two-stage technique was employed in which, (a) mixing of froth with solvent was carried out in a separate mixing device, and (b) the mixture was introduced into a separation apparatus, which enabled the withdrawal of separated solids, oil-solvent, and sludge phases to be made. The procedure outlined, here, was developed to evaluate the effect of chemicals, mechanical means, as well as the effect of some other process variables such as temperature, on overcoming the problem of membranes in dilution settling.

(2) Equipment

(a) Mixing

Initially, standard conditions of mixing involved a spatula rotated manually at 60 sps in a mixture of froth in solvent for 15 minutes, in a beaker. Other forms of mixing utilizing conventional mechanical stirring at various rotating speeds were also evaluated. The results of these mixing studies are discussed in the text. However, it should be noted that dis-solution of all oil in the solvent appeared to have occurred in less than 5 minutes.

(b) Separation

The mixture of froth and solvent was introduced into a laboratory separator. The apparatus is shown in Appendix, Figure 1. The vibrating screen had already been located at the surface of the lower aqueous phase, which occupied both the lower part of the upper chamber, as well as the lower chamber. The aqueous phase was either water, buffer, or a chemical solution. Solids and oil that separate into the water phase sank into the lower chamber. Withdrawal as a function of time was made, obtaining a progressive number of samples which were evaluated for weights of solids and oil removed. After each withdrawal the lower chamber was filled with process water or a chemical solution and vented through the 3-way valve separating the upper and the lower chambers. This technique proved very effective in withdrawal and elimination of air from the apparatus, which had disturbed the oil-water interface in the upper chamber in earlier apparatus design experiments.

A sample of oil-solvent was withdrawn at any depth or at any time from the upper phase. However, in most experiments the bulk (~95%) of the oil-solvent phase was removed using a syringe at the end of the experiment. The solids remaining in the sludge phase were computed by the difference. However, in every experiment the sludge phase was also removed and, in some cases, analyzed or further upgraded, e.g. centrifuging.

Other techniques of separation which were tried, involved the introduction of process water into the lower chamber and overflowing the oil-solvent phase from the top of the upper chamber. This enables the bulk of the oil-solvent phase to be recovered from the sludge as well as the separate recovery of the bulk of the sludge phase. However, the disadvantages of this type of withdrawal over that using a syringe, is in the loss of oil phase on the walls of the upper chamber above the oil-water interface, and excessive water content in the sludge.

(3) Summary

This developed technique proved most successful in evaluating the process variables of dilution settling on a small scale, in terms of solids transfer across a membrane emulsion at the oil-water interface. This operation was very consistent, and reproducibility was more a function of feed preparation and sampling.

V8-Figure 6

Small Scale Dilution Settling Apparatus

SETTLING

VIBRATION

ULTRASONICS

JIGGING

(5) Along the lines of forming a type of coacervate, a good quality froth was mixed with varsol, in some case, and with varsol and about 30% amyl alcohol in another. Pouring these mixtures into water, the following observations were made:

(a) in the case of just the varsol, three phases formed, an upper oil and solvent, a lower water and solids, and a large emulsion intermediate layer.

(b) when amyl alcohol was added to the varsol, the separation resulted in only two phases, an upper oil and solvents and a lower water and solids. It is probably that the upper oil layer contained the emulsion in a dispersed form by the action of the alcohol which partitions between the two phases. However, clean separation could be effected.

(c) (b) was repeated with a poor quality froth. Again, a big improvement was obtained , but only about 75% of the emulsion went into the oil phase with amyl alcohol addition.

In conclusion, it is believed that the skins discussed in Section 9, are similar to those stabilizing emulsions in solvent dilution and settling, i.e, polyvalent salts of the anionic surfactants, the polyvalent ion being either free or absorbed on a clay mineral or silica particle.

the approach should be to break those salts forming sodium soaps and free particles. This has been found to be best accomplished with sodium phosphates and silicates. The emulsion problem may be still further improved by the addition of organic surfactants, H.B 6-8 or 16-18, or alcohol.

VI. ACKNOWLEDGEMENTS

VI

ACKNOWLEDGMENTS

I wish to acknowledge

Dr. C.H. Caesar, Former Manager of the Research Department of Imperial Oil Ltd. at Sarnia, who first gave me the opportunity to carry out this fascinating research on the nature of oil sands.

Mr. J.L. Tiedge, former Manager of the Research Department of Imperial Oil Ltd. at Sarnia, who continued the support of my research.

Dr. C.W. Bowman, former Chairman of AOSTRA Edmonton, who encouraged me to record the details of this earlier work as a basis for others to build on, and with Dr. R.M. Butler, former Manager of Heavy Oil Research Division Calgary, contributed in the experimental development and small scale field demonstration of the Sand Reduction Process.

The late Dr. J. Schulman, Cambridge and Columbia Universities.

Dr. N.K. Adam, Cambridge/London Universities (England), my former Tutor

Dr. H. Gunning, University of Alberta, and

Dr. Leja, University of British Columbia,

who were all influential in my thinking and research efforts on the interfacial behaviour of oil sands.

Many Imperial Oil colleagues and technical assistants who contributed much in the actual carrying out of many of the experimental investigations. Also, many new members of the then recently formed Syncrude Research Department, whose eagerness to explore ideas toward a better understanding of oil sand separations I always found most stimulating.

Dr. K. Clark, pioneer of the Hot Water Separation Process at Bitumount, and Dr. G. Montgomery, developer of the Cold Water Process at Fort McMurray, whose earlier publications in the literature were valuable sources of information on oil sand processing.

N.L.C. - B.N.C.
3 3286 10664306 3

PUBLISHED BY:
Alberta
OIL SANDS TECHNOLOGY
AND RESEARCH AUTHORITY